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CHEMISTRY

Solved Papers
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Chemistry
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Concept Map

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Miraculous Cures for Some Common Serious Diseases

The largest study of its kind has confirmed that chances of Dementia and Alzheimer's disease double with vitamin D deficiency in older people. The elderly with low levels of vitamin D had 53% increased risk of developing Dementia and those severely deficient had a 125% increased risk.

People with lower levels of vitamin D were 70% more likely to develop Alzheimer's disease and those with severe deficiency of vitamin D were 120% more likely to develop the disease. These are the findings of Dr. David J. Llewellyn of the University of Exeter Medical School in the U.K. Even in India, those suffering from Arthritis are given high doses of vitamins to repair bone density.

Here is the miraculous cure for Arthritis, Rickets, Dementia and Alzheimer's disease. High doses of vitamin D is the answer. The best source of getting this medicine is just to expose oneself to sunlight daily. Walking in the sun will serve the double purpose of having exercise as well as free medicine. This is not new to India. Even in small villages in India, when children get Rickets (weak bones) and cannot use the legs, they are given a massage of the legs with cod liver oil and the legs are exposed to sunlight. They get cured in a few months and this is a common thing.

The miraculous cure is SUNLIGHT.

However, nature does not change us for sunlight. If only we care to tap our ancient wisdom, we can avoid many modern diseases.

The field for research is vast. We have to harvest it after hard work.

All our best wishes for our future scientists.

Anil Ahlawat
Editor

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CHEMISTRY Musing

Chemistry Musing was started from August '13 issue of Chemistry Today with the suggestion of Shri Mahabir Singh. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / AIPMT / AIIMS / Other PMTs & PETs with additional study material. In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / AIPMT. The detailed solutions of these problems will be published in next issue of Chemistry Today.

The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue.

We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

PROBLEM Set 14

JEE MAIN/PMTs

1. Consider the following pairs of gases A and B.

	A	B
(i)	CO ₂	N ₂ O
(ii)	CO	N ₂
(iii)	O ₂	O ₃
(iv)	H ₂ O	D ₂ O
(v)	²³⁵ UF ₆	²³⁸ UF ₆

Relative rates of effusion of gases A and B are in the order :

- (i) = (ii) < (v) < (iv) < (iii)
 - (i) = (ii) < (iii) < (iv) < (v)
 - (i) = (ii) < (iv) < (iii) < (v)
 - (i) < (ii) < (iii) < (iv) < (v)
2. Following statements regarding the periodic trends of chemical reactivity of the alkali metals and the halogens are given. Which of these statements gives the correct picture?
- The reactivity decreases in the alkali metals but increases in the halogens with increase in atomic number down the group.
 - In both the alkali metals and the halogens the chemical reactivity decreases with increase in atomic number down the group.

- Chemical reactivity increases with increase in atomic number down the group in both the alkali metals and halogens.
 - In alkali metals the reactivity increases but in the halogens it decreases with increase in atomic number down the group.
3. A 1 g sample of H₂O₂ solution containing x per cent H₂O₂ by weight required x mL of KMnO₄ for complete oxidation in acidic medium. The normality of KMnO₄ solution is
- 0.54 N
 - 9.60 N
 - 0.39 N
 - 0.59 N
4. Which of the following give benzoic acid on hydrolysis?
- Phenyl cyanide
 - Benzoyl chloride
 - Benzyl chloride
 - Methyl benzoate
- I, II, III only
 - II, III, IV only
 - II and IV only
 - I, II, IV only

Solution Senders of Chemistry Musing

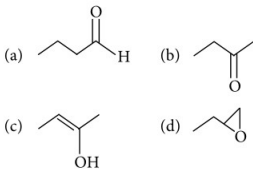
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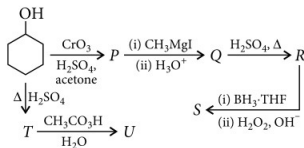
- Soumalya Pradhan, Midnapore (West Bengal)

5. Which of the following is not the functional isomer of the molecular formula C_4H_8O ?

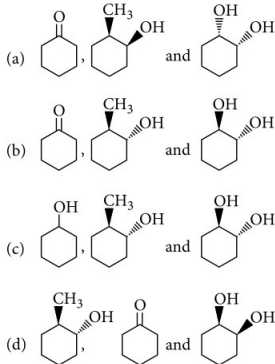


JEE ADVANCED

6. In the following series of reactions :

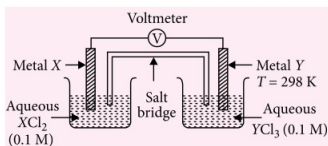
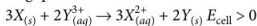


P, S and U are respectively



COMPREHENSION

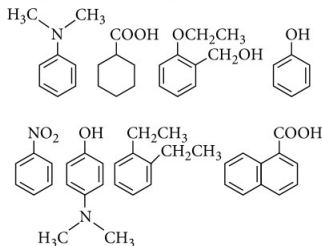
Based on the given information answer the following questions :



7. If $E_{X/X^{2+}}^{\circ} = 0.20 \text{ V}$, $E_{Y/Y^{3+}}^{\circ} = 0.40 \text{ V}$ then E_{cell}° of the above designed cell is
- (a) 0.60 V (b) -0.60 V
(c) 0.20 V (d) -0.20 V
8. E_{cell} of the given designed cell is
- (a) $\left(0.20 + \frac{0.0591}{2}\right) \text{ V}$
(b) $\left(-0.20 - \frac{0.0591}{3}\right) \text{ V}$
(c) $\left(-0.20 + \frac{0.0591}{6}\right) \text{ V}$
(d) +20 V

INTEGER VALUE

9. The enthalpy of formation of $\text{CO}_{2(g)}$, $\text{H}_2\text{O}_{(l)}$ and propene $_{(g)}$ are -393.5, -285.8 and 20.42 kJ mol⁻¹ respectively and the enthalpy of isomerisation of cyclopropane to propene is -33.0 kJ mol⁻¹ then the enthalpy change for the combustion of cyclopropane at 298 K is (in 10³ kJ mol⁻¹)
10. Amongst the following, the total number of compounds soluble in aqueous NaOH is





EXAMINER'S MIND NCERT^{CLASS} XI

The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XI. This year JEE (Main & Advanced) / AIPMT / AIIMS/other PMTs have drawn their papers heavily from NCERT books.

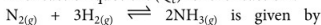
EQUILIBRIUM | REDOX REACTIONS

SECTION - I

Only One Option Correct Type

This section contains 20 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

1. The reaction quotient (Q_c) for the reaction :



$$Q_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

The reaction will proceed from right to left if

- (a) $Q_c = K_c$ (b) $Q_c < K_c$
(c) $Q_c > K_c$ (d) $Q_c = 0$
2. In an oxidation process for a cell,

$$\text{M}_1 \rightarrow \text{M}_1^{n+} + n\text{e}^-$$
the other metal (M_2) being univalent showing reduction takes up electrons to complete redox reaction.
(a) $(n-1)$ (b) 1
(c) n (d) 2
3. 0.6 mole of PCl_5 , 0.3 mole of PCl_3 and 0.5 mole of Cl_2 are taken in a 1 L flask to obtain the following equilibrium :

$$\text{PCl}_{5(g)} \rightleftharpoons \text{PCl}_{3(g)} + \text{Cl}_{2(g)}$$
If the equilibrium constant K_c for the reaction is 0.2. Predict the direction of the reaction.
(a) Forward direction
(b) Backward direction
(c) Direction of the reaction cannot be predicted
(d) Reaction does not move in any direction.
4. A compound contains atoms X, Y and Z. The oxidation number of X is +2, Y is +5 and Z is -2. The possible formula of the compound is

- (a) XYZ_2 (b) $\text{Y}_2(\text{XZ}_3)_2$
(c) $\text{X}_3(\text{YZ}_4)_2$ (d) $\text{X}_3(\text{Y}_4\text{Z}_2)$

5. N_2 and H_2 in 1 : 3 molar ratio are heated in a closed container having a catalyst. When the following equilibrium, $\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightleftharpoons 2\text{NH}_{3(g)}$ is attained, the total pressure is 10 atm and mole fraction of NH_3 is 0.60. The equilibrium constant K_p for dissociation of NH_3 is
(a) 1.33 (b) 0.75
(c) 0.57 (d) 2.33
6. After balancing the equation,

$$\text{K}_2\text{Cr}_2\text{O}_7 + x\text{H}_2\text{SO}_4 + y\text{SO}_2 \rightarrow \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + z\text{H}_2\text{O}$$
the values of x , y and z obtained will be respectively
(a) 1, 3, 1 (b) 2, 2, 1
(c) 1, 1, 3 (d) 1, 2, 1
7. In which of the following case, does the reaction go farthest to completion?
(a) $K = 10^{20}$ (b) $K = -20$
(c) $K = 10$ (d) $K = 1$
8. Using the standard electrode potential, find out the pair between which redox reaction is not feasible.
 E° values : $\text{Fe}^{3+}/\text{Fe}^{2+} = +0.77$; $\text{I}_2/\text{I}^- = +0.54$;
 $\text{Cu}^{2+}/\text{Cu} = +0.34$; $\text{Ag}^+/\text{Ag} = +0.80$ V
(a) Fe^{3+} and I^- (b) Ag^+ and Cu
(c) Fe^{3+} and Cu (d) Ag and Fe^{3+}
9. The solubility product of Ag_2CrO_4 is 32×10^{-12} . What is the concentration of CrO_4^{2-} ions in that solution?
(a) $8 \times 10^{-4} \text{ mol L}^{-1}$ (b) $16 \times 10^{-4} \text{ mol L}^{-1}$
(c) $2 \times 10^{-4} \text{ mol L}^{-1}$ (d) $8 \times 10^{-8} \text{ mol L}^{-1}$

10. Oxidation number of sulphur in Caro's acid is
 (a) +6 (b) +4
 (c) +8 (d) +7

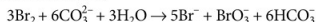
11. What is the correct sequence, to complete the paragraph?

According to Le Chatelier, if pressure is increased,

- (1) if pressure is decreased, the system will try to increase the pressure
 (2) the system will try to reduce the pressure
 (3) by favouring that reaction which is accompanied by a decrease in the number of moles
 (4) by favouring that reaction which is accompanied by an increase in the number of moles.

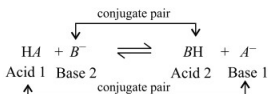
- (a) 2 3 1 4 (b) 1 2 3 4
 (c) 1 4 3 2 (d) 1 3 2 4

12. In the reaction :



- (a) Bromine is reduced and carbonate ion is oxidised.
 (b) Bromine undergoes disproportionation.
 (c) Bromine is reduced and water is oxidised.
 (d) Only water is oxidised to carbonic acid.

13. According to Bronsted-Lowry concept of acids and bases, a conjugate acid-base pair can exist as



Mark the option in which conjugate pair is not correctly matched.

Species Conjugate acid Conjugate base

- (a) HCO_3^- CO_3^{2-} H_2CO_3
 (b) HPO_4^{2-} H_2PO_4^- PO_4^{3-}
 (c) NH_3 NH_2^- NH_4^+
 (d) HS^- S^{2-} H_2S

14. Which of the following will act as cathode when connected to standard hydrogen electrode which has E° value given as zero?

- (i) Zn^{2+}/Zn , $E^\circ = -0.76 \text{ V}$
 (ii) Cu^{2+}/Cu , $E^\circ = +0.34 \text{ V}$

- (iii) Al^{3+}/Al , $E^\circ = -1.66 \text{ V}$

- (iv) $\text{Hg}_2^{2+}/\text{Hg}$, $E^\circ = +0.885 \text{ V}$

- (a) (i) and (ii) (b) (ii) and (iv)
 (c) (i) and (iii) (d) (i), (ii), (iii) and (iv)

15. The rate constant for the forward and backward reactions of hydrolysis of ester are 1.1×10^{-2} and 1.5×10^{-3} per minute respectively. The equilibrium constant of the reaction,
 $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}^+ \rightleftharpoons \text{CH}_3\text{COOH}$

+ $\text{C}_2\text{H}_5\text{OH}$ is

- (a) 7.75 (b) 6.33
 (c) 8.33 (d) 7.33

16. 3.92 g of ferrous ammonium sulphate was dissolved in 100 mL water. 20 mL of this solution requires 18 mL of potassium permanganate during titration for complete oxidation. The weight of KMnO_4 present in one litre of the solution is

- (a) 34.76 g (b) 12.38 g
 (c) 1.238 g (d) 3.51 g

17. Buffer solution can be obtained by mixing aqueous solution of

- (a) CH_3COONa and excess HCl
 (b) CH_3COONa and CH_3COOH
 (c) NaOH and NaCl
 (d) CH_3COOH and excess NaOH .

18. In which of the following compounds is iron in its least oxidation state?

- (a) $\text{K}_3[\text{Fe}(\text{OH})_6]$
 (b) $\text{K}_2[\text{FeO}_4]$
 (c) $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$
 (d) $[\text{Fe}(\text{CN})_6]^{3-}$

19. pK_a of a weak acid is 5.76 and pK_b of a weak base is 5.25. What will be the pH of the salt formed by the two?

- (a) 7.255 (b) 7.005
 (c) 10.225 (d) 4.255

20. Which of the following is a redox reaction?

- (a) $\text{BaCl}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{BaSO}_4 + 2\text{HCl}$
 (b) $\text{H}_2\text{SO}_4 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$
 (c) $\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} \rightarrow$
 $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$
 (d) $2\text{FeCl}_3 + \text{SnCl}_2 \rightarrow 2\text{FeCl}_2 + \text{SnCl}_4$

SECTION - II

One or More Options Correct Type

This section contains 5 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONE or MORE are correct.

21. Which of the following statements are correct?
- According to Bronsted—Lowry concept, H_2SO_4 can also act as a base.
 - SiF_4 is an acid according to Lewis concept.
 - Stronger the acid, higher is its $\text{p}K_a$ value.
 - HCl , HNO_3 and H_2SO_4 act as equally strong acids in any solvent.
22. In acidic medium, the equivalent weight of KMnO_4 is
- $M/6$
 - $M/5$
 - $M/4$
 - $M/3$
23. Which of the following aqueous solutions will have a pH less than 7.0?
- NH_4NO_3
 - NaOH
 - FeCl_3
 - Na_3PO_4
24. Which of the following elements show fractional oxidation state in any of their compounds?
- P
 - S
 - I
 - N
25. A reaction $\text{S}_{8(g)} \rightleftharpoons 4\text{S}_{2(g)}$ is carried out by taking 2 moles of $\text{S}_{8(g)}$ and 0.2 mole of $\text{S}_{2(g)}$ in a reaction vessel of 1 litre. Which are correct? ($K_c = 6.3 \times 10^{-6}$, $t = 627^\circ\text{C}$)
- Reaction quotient is 8×10^{-4} .
 - Reaction proceeds in backward direction.
 - $K_p = 2.54$
 - Reaction proceeds in forward direction.

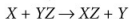
SECTION - III

Paragraph Type

This section contains 2 paragraphs each describing theory, experiment, data, etc. Six questions relate to two paragraphs with three questions on each paragraph. Each question of a paragraph has only one correct answer among the four choices (a), (b), (c) and (d).

Paragraph for Questions 26 to 28

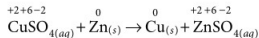
In a displacement reaction, an ion (or an atom) in a compound is replaced by an ion (or an atom) of another element. It may be denoted as :



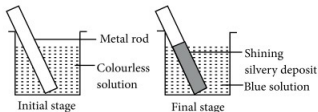
Metal displacement : A metal in a compound can be displaced by another metal in the uncombined state.

Non-metal displacement : The non-metal displacement redox reactions include hydrogen displacement and a rarely occurring reaction involving oxygen displacement.

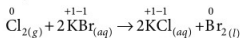
26. Given below is a redox reaction. Which of the following types the reaction belongs to?



- Combination reaction
 - Decomposition reaction
 - Metal displacement reaction
 - Non-metal displacement reaction
27. Identify the redox reaction taking place in a beaker.

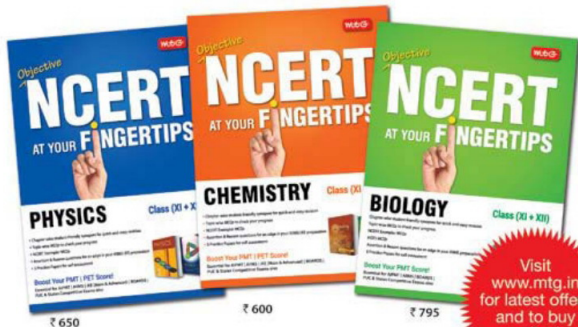


- $\text{Zn}_{(s)} + \text{Cu}^{2+}_{(aq)} \rightarrow \text{Zn}^{2+}_{(aq)} + \text{Cu}_{(s)}$
 - $\text{Cu}_{(s)} + 2\text{Ag}^{+}_{(aq)} \rightarrow \text{Cu}^{2+}_{(aq)} + 2\text{Ag}_{(s)}$
 - $\text{Cu}_{(s)} + \text{Zn}^{2+}_{(aq)} \rightarrow \text{Zn}_{(s)} + \text{Cu}^{2+}_{(aq)}$
 - $2\text{Ag}_{(s)} + \text{Cu}^{2+}_{(aq)} \rightarrow 2\text{Ag}^{+}_{(aq)} + \text{Cu}_{(s)}$
28. Which type of redox reaction is shown by the following reaction?



- Decomposition reaction
- Metal displacement reaction
- Non-metal displacement reaction
- Disproportionation reaction

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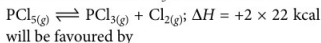
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Paragraph for Questions 29 to 31

"Le Chatelier's principle states that a change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner so as to reduce or to counteract the effect of the change". This is applicable to all physical and chemical equilibria.

29. The dissociation of PCl_5 in the reaction :

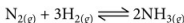


- increasing temperature
- increasing pressure
- adding more PCl_3
- adding more Cl_2 .

30. In which of the following reactions, the increase in pressure will favour the increase in products?

- $\text{N}_{2(g)} + \text{O}_{2(g)} \rightleftharpoons 2\text{NO}_{(g)}$
- $\text{PCl}_{3(g)} + \text{Cl}_{2(g)} \rightleftharpoons \text{PCl}_{5(g)}$
- $\text{PCl}_{5(g)} \rightleftharpoons \text{PCl}_{3(g)} + \text{Cl}_{2(g)}$
- $2\text{CO}_{2(g)} \rightleftharpoons 2\text{CO}_{(g)} + \text{O}_{2(g)}$

31. On increasing the pressure, in which direction will the gas phase reaction proceed to re-establish equilibrium, is predicted by applying the Le Chatelier's principle. Consider the reaction :



Which of the following is correct, if the total pressure at which the equilibrium is established, is increased without changing the temperature?

- K will remain same.
- K will decrease.
- K will increase.
- K will increase initially and decrease when pressure is very high.

SECTION - IV

Matching List Type

This section contains 3 multiple choice questions. Each question has matching lists. The codes for the lists have choices (a), (b), (c) and (d), out of which ONLY one is correct.

32. Match the List I with List II and select the correct answer using the code given below the lists :

List I

List II

- | | |
|---|------------------|
| P. $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}_{(aq)}$ | 1. Brønsted base |
| Q. Salt of weak acid and strong base | 2. Neutral base |
| R. H_2PO_4^- | 3. Basic |
| S. Solution of pH 6.5 at high temperature | 4. Acidic |
- | | P | Q | R | S |
|-----|---|---|---|---|
| (a) | 3 | 4 | 2 | 1 |
| (b) | 2 | 1 | 4 | 3 |
| (c) | 4 | 3 | 1 | 2 |
| (d) | 1 | 2 | 3 | 4 |

33. Match the List I with List II and select the correct answer using the code given below the lists :

List I

List II

- | | |
|---|--|
| P. $[\text{A}^{+}]^x [\text{B}^{-}]^y > K_{sp}$ | 1. Precipitation just starts |
| Q. $[\text{A}^{+}]^x [\text{B}^{-}]^y < K_{sp}$ | 2. Buffer capacity |
| R. $[\text{A}^{+}]^x [\text{B}^{-}]^y = K_{sp}$ | 3. The solid A_xB_y will precipitate out |
| S. $d(b)/d(\text{pH})$ | 4. No precipitation |
- | | P | Q | R | S |
|-----|---|---|---|---|
| (a) | 3 | 4 | 1 | 2 |
| (b) | 2 | 1 | 4 | 3 |
| (c) | 1 | 2 | 3 | 4 |
| (d) | 3 | 4 | 2 | 1 |

34. Match the List I with List II and select the correct answer using the code given below the lists :

List I

List II

- | | |
|--|-----------------------|
| P. $2\text{Cu}^+ \rightarrow \text{Cu}^{++} + \text{Cu}$ | 1. Auto oxidation |
| Q. $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$ | 2. Redox reaction |
| R. $\text{PbO}_2 + \text{H}_2\text{O} \rightarrow \text{PbO} + \text{H}_2\text{O}_2$ | 3. Neutralisation |
| S. $\text{Zn} + 2\text{HCl} \rightarrow \text{ZnCl}_2 + \text{H}_2$ | 4. Disproportionation |

	P	Q	R	S
(a)	3	4	1	2
(b)	2	1	4	3
(c)	1	2	3	4
(d)	4	3	1	2

SECTION - V

Assertion-Reason Type

In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
- (b) If both assertion and reason are true but reason is not the correct explanation of assertion.
- (c) If assertion is true but reason is false.
- (d) If both assertion and reason are false.

35. Assertion : If reaction quotient, Q_c for a particular reaction is greater than K_c , the reaction will proceed in the direction of reactants.

Reason : Reaction quotient is defined in the same way as the equilibrium constant K_c except that the concentrations in Q_c are not necessarily equilibrium values.

36. Assertion : In ClF_3 , fluorine has the oxidation number -1.

Reason : Electron affinity of chlorine is greater than that of fluorine.

37. Assertion : pH of the buffer solution is not affected by dilution.

Reason : $\text{pH} = \text{p}K_a +$

$$\log \frac{[\text{Conjugate acid, } BH^+]}{[\text{Base, } B]}$$

38. Assertion : Oxygen atom in both, O_2 and O_3 has an oxidation number of -2.

Reason : Oxygen is assigned an oxidation number -2 in all of its compounds.

39. Assertion : The strength of haloacids increases in the order : $\text{HI} \ll \text{HBr} \ll \text{HCl} \ll \text{HF}$.

Reason : Strength of acid HA depends only on the electronegativity difference between H and A.

40. Assertion : F_2 undergoes disproportionation reactions.

Reason : Fluorine shows only 0 and -1 oxidation states.

SECTION - VI

Integer Value Correct Type

This section contains 10 questions. The answer to each question is a single digit integer, ranging from 0 to 9 (both inclusive).

41. The pH at which $\text{Mg}(\text{OH})_2$ begins to precipitate from a solution containing 0.1 M Mg^{2+} ions is (K_{sp} of $\text{Mg}(\text{OH})_2 = 1 \times 10^{-11}$)

42. The oxidation number of Mn in the product of alkaline oxidative fusion of MnO_2 is

43. A sample of pure PCl_5 was introduced into an evacuated vessel at 473 K. After equilibrium was attained, concentration of PCl_5 was found to be $0.5 \times 10^{-1} \text{ M}$ and that of PCl_3 to be $x \times 10^{-2}$. If the value of K_c is 8.3×10^{-3} , then the value of x is

44. In the reaction, $\text{PbS} + \text{H}_2\text{O}_2 \rightarrow \text{PbSO}_4 + \text{H}_2\text{O}$ the increase in oxidation state of S will be

45. In an experiment starting with 1 mole of ethyl alcohol, 1 mole of acetic acid and 1 mole of water at 100°C , the equilibrium mixture on analysis shows that 54.3% of the acid is esterified. The equilibrium constant of this reaction is

46. The number of moles of oxalate ions oxidized by one mole of MnO_4^- ion is x/y . The value of $(x + y)$ is

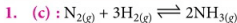
47. For the reaction, $\text{I}_{2(g)} + \text{H}_{2(g)} \rightleftharpoons 2\text{HI}_{(g)}$. If $K_p = K_c$, then the value of Δn is

48. In the ionic equation : $\text{BiO}_3^- + 6\text{H}^+ + x e^- \longrightarrow \text{Bi}^{3+} + 3\text{H}_2\text{O}$ the value of x is

49. If concentrations of SO_2 and O_2 in the equilibrium reaction, $2\text{SO}_{2(g)} + \text{O}_{2(g)} \rightleftharpoons 2\text{SO}_{3(g)}$ are quadrupled, the concentration of SO_3 now will be times.

50. The oxidation number of Fe in $\text{K}_4[\text{Fe}(\text{CN})_6]$ is

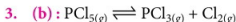
SOLUTIONS



$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}; \Delta n = 2 - 4 = -2$$

Thus, the reaction will proceed in reverse direction when $Q_c > K_c$.

2. (c) : The reaction shows $M_2^{n+} + ne^- \rightarrow M_2$
i.e. electrons released at anode
= electrons used at cathode.



$$Q_c = \frac{0.5 \times 0.3}{0.6} = 0.25$$

$K_c = 0.2$. Since $Q_c > K_c$, the reaction will proceed in backward direction.

4. (c) : Sum of the oxidation numbers of atoms in it, is zero.



Initially 1 3 0
At equilibrium $1 - \alpha$ $3 - 3\alpha$ 2α
Total moles = $1 - \alpha + 3 - 3\alpha + 2\alpha = 4 - 2\alpha$

$$\therefore x_{NH_3} = \frac{2\alpha}{4 - 2\alpha} = 0.6$$

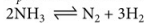
$$\Rightarrow \frac{\alpha}{2 - \alpha} = 0.6 \Rightarrow \alpha = 1.2 - 0.6\alpha$$

$$\Rightarrow 1.6\alpha = 1.2 \Rightarrow \alpha = \frac{3}{4} = 0.75$$

$$\therefore x_{N_2} = \frac{1 - \alpha}{4 - 2\alpha} = \frac{0.25}{2.5} = \frac{1}{10}$$

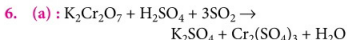
$$x_{H_2} = \frac{3 - 3\alpha}{4 - 2\alpha} = \frac{3(0.25)}{2(1.25)} = 0.3$$

K_p for the reverse reaction



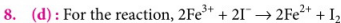
$$K'_p = \frac{(p_{N_2})(p_{H_2})^3}{(p_{NH_3})^2} = \frac{(0.1 \times 10)(0.3 \times 10)^3}{(0.6 \times 10)^2}$$

$$= \frac{3^3}{6^2} = 0.75$$



So, $x = 1, y = 3, z = 1$.

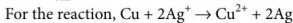
7. (a) : Larger the value of equilibrium constant farther the reaction goes to completion.



$$E_{cell}^{\circ} = E_{Fe^{3+}/Fe^{2+}}^{\circ} - E_{I_2/I^-}^{\circ}$$

$$= 0.77 - (0.54) = +0.23 V$$

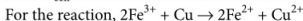
Here, E_{cell}° is +ve, so reaction is feasible.



$$E_{cell}^{\circ} = E_{Ag^+/Ag}^{\circ} - E_{Cu^{2+}/Cu}^{\circ}$$

$$= 0.80 - (0.34) = +0.46 V$$

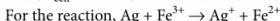
Here, E_{cell}° is +ve so, the reaction is feasible.



$$E_{cell}^{\circ} = E_{Fe^{3+}/Fe^{2+}}^{\circ} - E_{Cu^{2+}/Cu}^{\circ}$$

$$= 0.77 - (0.34) = +0.43 V$$

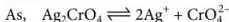
Here, E_{cell}° is +ve so, the reaction is feasible.



$$E_{cell}^{\circ} = E_{Fe^{3+}/Fe^{2+}}^{\circ} - E_{Ag^+/Ag}^{\circ} = 0.77 - (0.80) = -0.03 V$$

Here, E_{cell}° is negative, so the reaction is not feasible.

9. (c) : The solubility product of Ag_2CrO_4 is given as 32×10^{-12} .



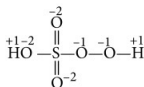
Let the solubility of Ag_2CrO_4 be x , the solubility of Ag^+ and CrO_4^{2-} is also x .

$$\Rightarrow \text{Solubility product } (K_{sp}) = (2x)^2 x = 4x^3$$

$$\Rightarrow 4x^3 = 32 \times 10^{-12}$$

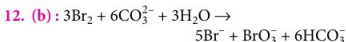
$$\Rightarrow x = 2 \times 10^{-4} \text{ mol L}^{-1}$$

10. (a) : Caro's acid is H_2SO_5 .

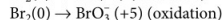
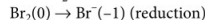


\therefore Sulphur is having +6 oxidation state.

11. (a)



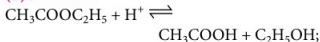
Here Br_2 is both reduced and oxidized.



13. (b)

14. (b) : When the value of standard reduction potential is positive, the electrode undergoes reduction and acts as cathode.

15. (d) : Reaction



Rate constant for forward reaction (k_f) = 1.1×10^{-2} per minute and rate constant for backward reaction (k_b) = 1.5×10^{-3} per minute. The equilibrium constant

$$K_c = \frac{k_f}{k_b} = \frac{1.1 \times 10^{-2}}{1.5 \times 10^{-3}} = 7.33$$

16. (d) : The redox reaction involving the oxidation of Fe^{2+} (from ferrous ammonium sulphate) is $\text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \longrightarrow 5\text{Fe}^{3+} + \text{Mn}^{2+} + 4\text{H}_2\text{O}$. Mol. wt. of ferrous ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O} = 392$

$$\therefore \text{Molarity of } (\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O} = \frac{\text{Wt.}}{\text{Mol. wt.}} \times \frac{1000}{\text{Volume}} = \frac{3.92}{392} \times \frac{1000}{100} = 0.1$$

Applying molarity equation,

$$\frac{M_1 V_1}{n_1} (\text{Ferrous ammonium sulphate}) = \frac{M_2 V_2}{n_2} (\text{KMnO}_4)$$

$$\text{or } \frac{0.1 \times 20}{5} = \frac{M_2 \times 18}{1} \text{ or } M_2 = \frac{0.1 \times 20}{5 \times 18} = \frac{1}{45}$$

Amount of KMnO_4 present in one litre

$$= \text{Molarity} \times \text{Mol. wt.} = \frac{1}{45} \times 158 = 3.51 \text{ g}$$

17. (b) 18. (c)

19. (a) : $\text{pH} = 7 + \frac{1}{2} [\text{p}K_a - \text{p}K_b]$

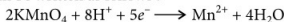
$$\text{pH} = 7 + \frac{1}{2} (5.76 - 5.25) = 7.255$$

20. (d)

21. (a, b) : (a) is correct because in presence of HClO_4 , H_2SO_4 can accept a proton and hence can act as a base.

(b) Si has empty d -orbitals to accept electrons. Hence, SiF_4 is a Lewis acid.

22. (b) : The reaction of KMnO_4 in acidic medium can be written as follows :



In the above reaction, the oxidation state of Mn changes from +7 to +2, thus, there is a $5e^-$ change.

\therefore Equivalent weight of KMnO_4 (in acidic medium) = $M/5$.

23. (a, c) : NH_4NO_3 and FeCl_3 are salts of strong acid and weak base, which on hydrolysis produce acidic solution i.e. $\text{pH} < 7.0$

24. (c, d) : I in KI_3 and N in N_3H shows fractional oxidation state.

25. (a, b, c) :

$$Q = \frac{[\text{S}_2]_t^4}{[\text{S}_8]_t} = \frac{(0.2)^4}{(2)} = 8 \times 10^{-4}, K_c = 6.3 \times 10^{-6}$$

$$\Delta n = 4 - 1 = 3$$

$$K_p = K_c \times (RT)^{\Delta n} = 6.3 \times 10^{-6} \times (0.0821 \times 900)^3 = 2.54$$

Reaction proceeds in backward direction since $Q > K_c$.

26. (c)

27. (b) : Since, copper is more reactive than silver, it displaces Ag^+ ions from its salt solution which get deposited on the copper rod.

28. (c)

29. (a) : As the reaction is endothermic and accompanied by an increase in volume, according to Le Chatelier's principle favourable conditions for dissociation of PCl_5 are increase in temperature and decrease in pressure.

30. (b) : Decrease in number of moles in the reaction makes it favourable at high pressure.

31. (a) : Equilibrium constant (K) is temperature dependent. Since, temperature is constant, K will remain same.

32. (c) : (P) $\text{Al}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_3 + 3\text{H}^+$
(Cationic hydrolysis, acidic)

(Q) In solution, $[\text{OH}^-] > [\text{H}^+]$ so it is basic. Since, K_a and K_b values are not given. So, pH of such solution cannot be predicted.

(R) Brønsted bases are proton acceptors.

(S) K_w value increases with increase in temperature. This means that the neutral solution at 60°C have a pH 6.5 instead of 7.0 and the pH scale lies in between 0 to 13.

33. (a) : (P) If $[\text{A}^{y+}][\text{B}^{x-}]^y > K_{sp}$, solid A_xB_y will precipitate out.

(Q) If $[\text{A}^{y+}]^x[\text{B}^{x-}]^y < K_{sp}$, no precipitation occurs.

(R) Precipitation just starts when $K_{\text{ions}} = K_{sp}$

(S) Buffer capacity = $\frac{d(b)}{d(\text{pH})}$

34. (d)

35. (b): If $Q_c > K_c$, then Q_c will tend to decrease so as to become equal to K_c . As a result, the reaction will proceed in the backward direction.

36. (b): More electronegative atom takes the negative oxidation state.

37. (a): pH of the buffer solution is not affected by dilution because ratio under the logarithmic term remains unchanged.

38. (d): Elements in the free state exhibit an oxidation number of zero.

Oxidation number of oxygen in most of its compounds is -2 with two exceptions: in peroxides, oxidation number of oxygen is -1 and in superoxides, oxidation number of oxygen is $-\frac{1}{2}$.

39. (d): The correct order of acidic strength is $\text{HF} \ll \text{HCl} \ll \text{HBr} \ll \text{HI}$. While comparing elements in the same group of the periodic table, H—A bond strength is a more important factor in determining acidity than its polar nature. As the size of A increases down the group, H—A bond strength decreases and the acid strength increases.

40. (c)

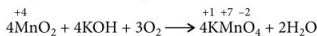
41. (9): K_{sp} of $\text{Mg}(\text{OH})_2 = 1 \times 10^{-11} = [\text{Mg}^{2+}][\text{OH}^-]^2$

$$[\text{OH}^-]^2 = \frac{1 \times 10^{-11}}{0.1} = 1 \times 10^{-10}$$

$$[\text{OH}^-] = 1 \times 10^{-5}; [\text{H}^+] = \frac{1 \times 10^{-14}}{1 \times 10^{-5}} = 1 \times 10^{-9}$$

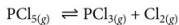
$$\text{pH} = -\log [\text{H}^+] = -\log (1 \times 10^{-9}) = 9$$

42. (7): The balanced equation is



Thus, O.N. of Mn in KMnO_4 is 7.

43. (2): Let the concentrations of both PCl_3 and Cl_2 at equilibrium be x M. The given reaction is



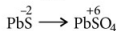
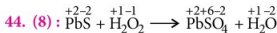
Concentration at equilibrium $0.5 \times 10^{-1} \quad x \quad x$

$$\text{Now, } K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$$

$$\text{Therefore, } \frac{x \times x}{0.5 \times 10^{-1}} = 8.3 \times 10^{-3}$$

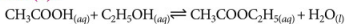
$$\text{or } x^2 = 4.15 \times 10^{-4}$$

$$\text{which gives } x = 2.04 \times 10^{-2} \text{ M}$$



So, increase in oxidation number of S = 8 units per PbS molecule.

45. (4):



Initial	1	1	0	1
At equil.	$1 - x$	$1 - x$	x	$1 + x$

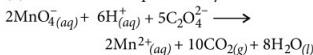
Given, $x = 0.543$

$$1 - 0.543 \quad 1 - 0.543 \quad 0.543 \quad 1 + 0.543$$

Applying law of mass action,

$$K_c = \frac{[\text{Ester}][\text{Water}]}{[\text{Acid}][\text{Alcohol}]} = \frac{0.543 \times 1.543}{0.457 \times 0.457} = 4.012$$

46. (7): The balanced equation may be written as:



Now, as 2 moles of MnO_4^- oxidizes 5 moles of $\text{C}_2\text{O}_4^{2-}$.

So, 1 mole of MnO_4^- will oxidize

$$\frac{5}{2} \text{ moles of } \text{C}_2\text{O}_4^{2-}$$

$$\text{i.e., } x = 5 \text{ and } y = 2$$

$$\therefore (x + y) = 5 + 2 = 7$$

47. (0)

48. (2)

$$49. (8): K = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = \frac{c^2}{a^2b}$$

On making the concentration of SO_2 and O_2 four times, suppose $[\text{SO}_3]$ becomes x times. Then

$$K = \frac{(xc)^2}{(4a)^2(4b)} = \frac{x^2c^2}{64a^2b}$$

$$\text{As } K \text{ remains constant } \frac{x^2c^2}{64a^2b} = \frac{c^2}{a^2b}$$

$$\text{or } x^2 = 64 \text{ or } x = 8$$

50. (2)





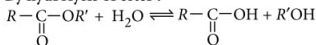
CONCEPT BOOSTER

Dear students second part of the Carboxylic Acids and their Derivatives is here. "Definiteness of purpose is the starting point of all achievement" this is a fact. Students, this is applicable in all aspects of our lives. Hope you all follow a target and give your best to achieve this. Like my all other articles, this article is also devoted to show you the approach how you should take your preparation a neat and clean path with clear conceptions. Take care and good bye!!!

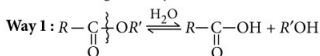
*Arunava Sarkar

General Methods of Preparation of Aliphatic and Aromatic Carboxylic Acids

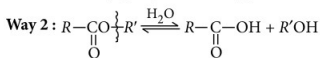
By hydrolysis of ester :



Different mechanisms have been put forward because the above reaction is possible in either of the following two ways :



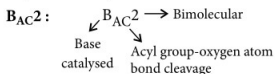
Here the cleavage of bond is taking place in between the acyl group and the oxygen atom.



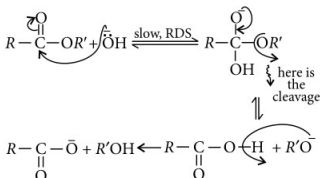
Here the cleavage of bond is taking place in between the oxygen atom and the alkyl group. Moreover, hydrolysis of ester can either be acid or base catalysed and it may either be unimolecular or bimolecular reaction.

Overall eight possible mechanisms are there :

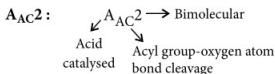
(1) B_{AC}1 (2) B_{AC}2 (3) A_{AC}1 (4) A_{AC}2
(5) B_{AL}1 (6) B_{AL}2 (7) A_{AL}1 (8) A_{AL}2
Out of these eight mechanisms, B_{AC}1 and A_{AL}2 have not been observed. Even within the rest six, few are very rare.



The reaction can be shown as :

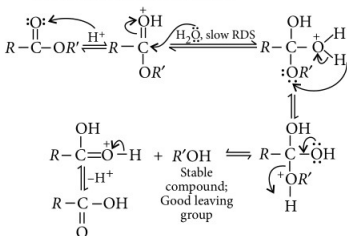


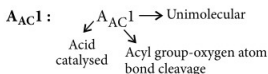
This reaction is a kind of addition-elimination reaction and here —OR' group is being substituted by —OH group.



This reaction is quite common.

The reaction can be shown as :

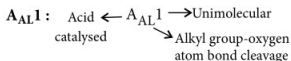
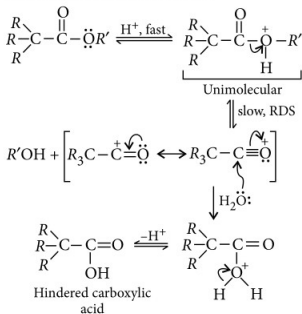




Basically, this mechanism is applicable for a sterically hindered ester.

H⁺ does not attack on double bonded oxygen atom as it is sterically hindered and moreover the +I effect of three alkyl groups stabilise the acylium ion

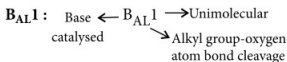
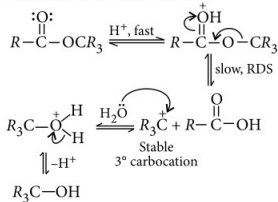
The reaction can be shown as :



This is possible when the alkyl group attached with the oxygen atom is very much stabilized like 3° carboanion.

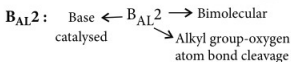
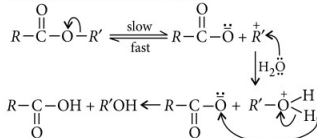
The attack is not at the oxygen atom of —OCR₃ because this oxygen atom is sterically hindered.

The reaction can be shown as :



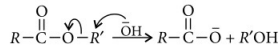
This occurs only at very special cases. Though it is base catalysed but in fact the solution becomes very weakly alkaline or even it is kept neutral. The basic norm for the success of the reaction is that the solvent should have high ionizing power so that the ester molecule itself can undergo ionization.

The reaction can be shown as :

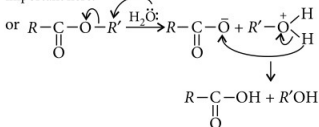


Here, slightly alkaline solution (or even the neutral solution promotes the reaction).

The reaction can be shown as :



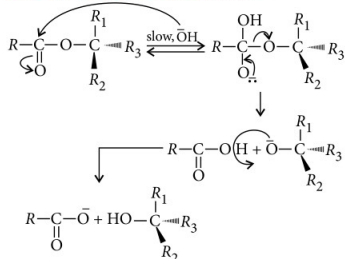
Solvent's ionization power is again very important here.



Synopsis of the whole hydrolysis process :

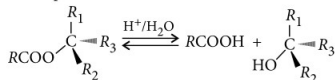
Type	Observation
B _{AC} 1	Not observed
B _{AC} 2	Very much observed
A _{AC} 1	Special cases
A _{AC} 2	Very much observed
B _{AL} 1	Special cases
B _{AL} 2	Rarely observed
A _{AL} 1	Very common for 3° alcohols
A _{AL} 2	Not observed

Stereochemistry of B_{AC}2 Mechanism



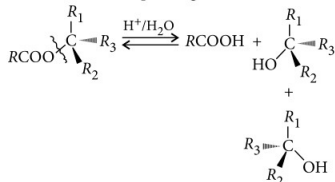
Stereochemistry of A_{AC}2 Mechanism

Here also the retention of configuration at the alcohol portion is maintained.



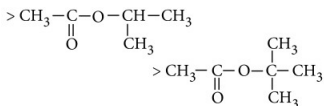
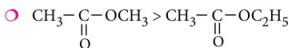
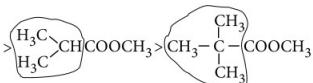
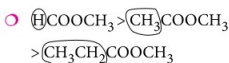
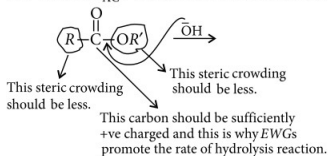
Stereochemistry of A_{AL}1 Mechanism

A stable carbocation is formed here which on attack by the nucleophile ($\text{H}_2\ddot{\text{O}}$) can generate the racemic mixture of the corresponding alcohol.

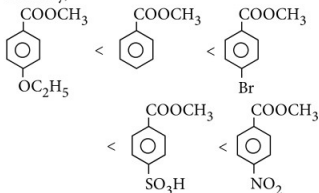


Rate of Different Esters in Hydrolysis Reaction

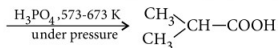
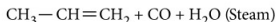
The case of B_{AC}2 mechanism is mentioned here.



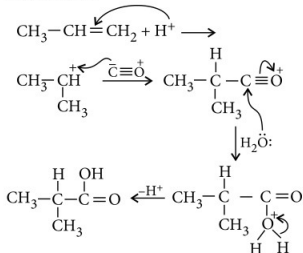
○ Similarly,



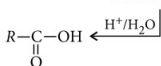
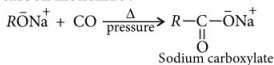
Koch Reaction :



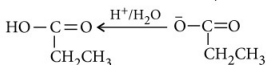
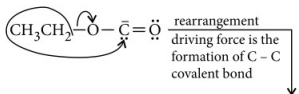
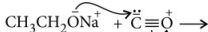
Mechanism :



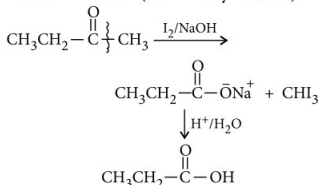
❑ **Reaction between sodium alkoxide and carbon monoxide :**



Mechanism :

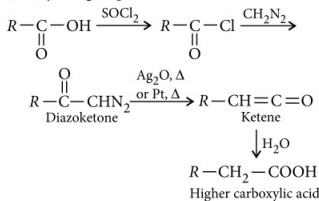


❑ **Haloform reaction (from methyl ketones) :**

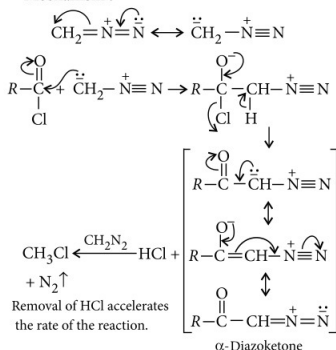


❑ **Arndt-Eistert Synthesis (via Wolff rearrangement) :**

The basic usefulness of the reaction is that it helps to increase the length of the carboxylic acid by the introduction of $-\text{CH}_2-$ group (methylene group).

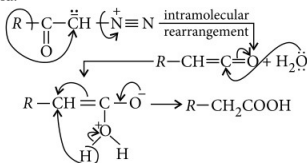


Mechanism :

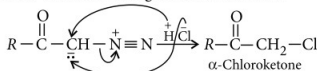


Removal of HCl accelerates the rate of the reaction.

α -Diazoketone when heated with silver oxide then it loses a molecule of N_2 (good leaving group). The carbene thus produced, rearranges itself through 1,2-shift of alkyl group and produced a ketene. This rearrangement is known as Wolff rearrangement. The ketene finally gets hydrolysed to give carboxylic acid.



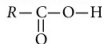
In the whole process, diazomethane is used in excess amount so that HCl can be removed because presence of HCl hampers the reaction by reacting with α -diazoketone to give α -chloroketone.



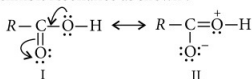
Acidic Property of Carboxylic Acids

Carboxylic acids are the organic acids.

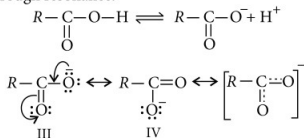
Carboxylic acids have the following structure :



It can exhibit resonance as shown :



Due to the +ve charge on the oxygen atom in the structure (II), O—H bond weakens and release of H^+ becomes easy. Moreover, after release of H^+ , the carboxylate ion that is produced is better stabilized through resonance.



This is why the carboxylic acids can easily release H^+ .

Why it is said that the carboxylate ion is better resonance stabilized than carboxylic acid?

This is mainly due to two reasons :

1. In structures (III) and (IV), there is no charge separation.
2. Structures (III) and (IV) are equivalent whereas structures (I) and (II) are not equivalent.

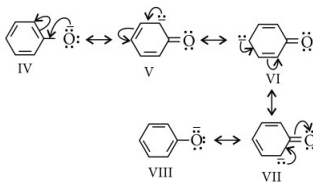
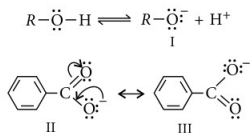
In carboxylate ion, the bond order of carbon-oxygen bond is $\frac{2+1}{2} = 1.5$ and therefore its bond length is in between $\text{C}=\text{O}$ and $\text{C}-\text{O}$ bond length.

Comparison of Acidity of Carboxylic Acids, Phenols and Alcohols

In general, acidity order is

Carboxylic acid > Phenol > Alcohol

The whole idea is based on resonance, i.e., stabilization of the conjugate base formed from them.

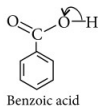


Alkoxide ion ($\text{R}-\ddot{\text{O}}^-$) is not at all resonance stabilized. So, the corresponding alcohol is the weakest among these three.

In structures (V), (VI), (VII), there is a -ve charge on the less electronegative carbon atom whereas in structures (II) and (III) which are equivalent structures, -ve charge is there on the oxygen atom. Now, in the structures (IV) and (VIII) where the -ve charge is on the oxygen atom only and if compared with structures (II) and (III) then it is observed that in structures (II) and (III), electrons are delocalized whereas it is localized in case of (IV) and (VIII) on the single oxygen atom. This is why carboxylate ion is better resonance stabilized than the phenoxide ion and carboxylic acid is stronger acid than phenol.

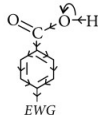
Role of electron donating and electron withdrawing groups on the acidity of carboxylic acids

Presence of Electron Withdrawing Group (EWG)



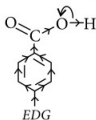
Benzoic acid

It is an acid because the oxygen atom withdraws the bonding electron pair involved in the covalent bond formation with hydrogen atom towards itself due to its higher electronegativity. As a consequence, $-\text{O}-\text{H}$ bond breaks and H^+ releases. Now, if an EWG will be present anywhere at the ring the scenario will be as below :



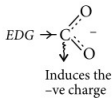
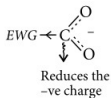
Here, *EWG* creates a deficiency of electron in the benzene ring and also helps to break the bond between oxygen and hydrogen. As a result $\text{—O} \overset{\curvearrowright}{\text{—}} \text{H}$ bond breaking rate is accelerated and release of H^+ is also accelerated. Thus, acidity increases.

Presence of Electron Donating Group (EDG)

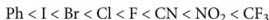


EDG wants to push the electron groups pair towards the hydrogen *i.e.* it wants to work against the pull of oxygen atom. Thus, breaking of $\text{—O} \overset{\curvearrowright}{\text{—}} \text{H}$ bond is hindered and the rate of H^+ release is retarded. Thus acidity decreases.

After the release of H^+ , the carboxylate ion that is produced is stabilized by *EWG* but destabilized by *EDG*.

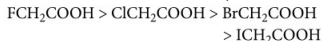


Following is the order of $-I$ effect of different groups :

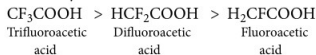


DISCUSSION FOR ALIPHATIC CARBOXYLIC ACIDS

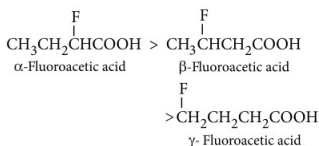
- **Nature of the group :** More powerful will be the *EWG*, more will be the acidity.



- **Number of the groups :** More will be the number of *EWG*, more will be the acidity while more will be the number of *EDG*, less will be the acidity.



- **Position of the group :** Whatever be the group whether *EDG* or *EWG* if it will be at a closed position to the —COOH group it can show its effect immensely.

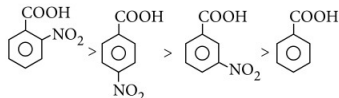


DISCUSSION FOR AROMATIC CARBOXYLIC ACIDS

Ortho effect operates here. *o*-Substituted benzoic acids are stronger than the *m*- or *p*-substituted benzoic acid. *Ortho* effect does not depend on the electron donating or electron withdrawing nature of the group.

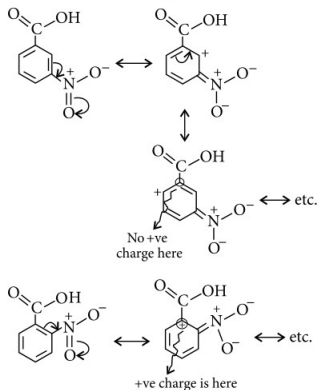
Nitrobenzoic Acid

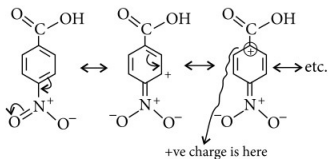
The order of acidity is found as follows :



($pK_a = 2.16$) ($pK_a = 3.41$) ($pK_a = 3.46$) ($pK_a = 4.19$)

—NO_2 group has $-I$ as well as $-R$ effect. Overall, —NO_2 group is very powerful *EWG*. —NO_2 group (or even any other group) cannot exert $-R$ effect (or even $+R$ effect) at the *meta* position.





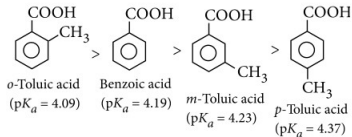
When the carbon atom of the ring with which $-\text{COOH}$ group is attached bears a +ve charge then the $-R$ effect is operative here and acidity is very much intensified here.

As, $-\text{NO}_2$ group is electron withdrawing therefore, all the nitro substituted benzoic acids are stronger than the benzoic acid. *Ortho*-nitrobenzoic acid is strongest because of the *ortho* effect as well as due to the fact that at *ortho* position $-I$ effect is stronger than that of the *meta* and *para* positions.

Among *meta* and *para*, *para* is stronger because at *meta* only $-I$ effect operates, however, at *para* both $-I$ and $-R$ effects operate.

Toluic Acid

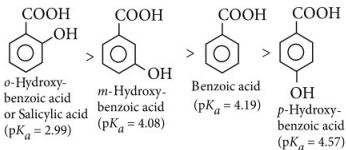
The order of acidity is found as follows :



Generally, $-\text{CH}_3$ group has $+I$ effect and can also exert hyperconjugation effect. Both the effects are electron donating. So all the $-\text{CH}_3$ substituted benzoic acids should be less acidic than benzoic acid. But due to *ortho* effect, *o*-toluic acid is strongest acid than benzoic acid. Among *meta* and *para*, *meta* is stronger acid as here hyperconjugation does not operate. Therefore, at *meta* overall electron donation is lesser than that at the *para*.

Hydroxybenzoic Acid

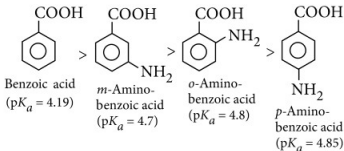
The order of acidity is found as follows :



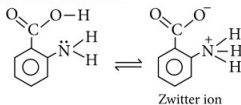
$-\text{OH}$ group has both $+R$ and $-I$ effects but $+R$ effect is found to be slightly dominating over the $-I$ effect. Due to *ortho* effect, *o*-hydroxybenzoic acid is found to be the strongest. At *meta* position only $-I$ effect operates, $+R$ effect does not operate. So, *m*-hydroxybenzoic acid is stronger than *p*-hydroxybenzoic acid and benzoic acid. Due to stronger $+R$ effect, *p*-hydroxybenzoic acid is weaker than benzoic acid.

Aminobenzoic Acid

The order of acidity is found as follows :



$-\text{NH}_2$ group has a very strong $+R$ effect and comparatively weaker $-I$ effect. So, all the aminobenzoic acids should be weaker than benzoic acid. But what about *ortho* effect? *Ortho* effect is very much reduced here because of the formation of Zwitter ion as follows :



mtg

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The H^+ released is trapped by $-\ddot{N}H_2$ group. This is why *o*-aminobenzoic acid takes the third position in the order. But if $-\ddot{N}H_2$ has a stronger $+R$ effect and weaker $-I$ effect, i.e. overall it is electron donating, then *m*-aminobenzoic acid should be more acidic than benzoic acid as at *m*-position, $+R$ effect does not operate. But it is found to be less acidic than benzoic acid.

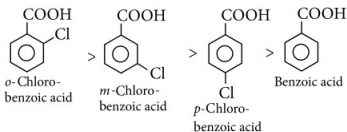
Basically, it can be explained as below :

The lone pair over the nitrogen atom in $-\ddot{N}H_2$ group makes it basic. As the lone pair is present, it makes the molecular atmosphere basic and the acidity of the carboxylic acid gets somehow reduced.

Halobenzoic Acid

Halogen atoms have very strong $-I$ effect and a weak $+R$ effect. This is why all halobenzoic acids are found to be stronger than benzoic acid.

The order of acidity is found as follows :



o-Chlorobenzoic acid is taking the first position because of the *ortho* effect and strongest $-I$ effect (least distance from $-\text{COOH}$ group). *meta* is taking the second position because at *meta* $+R$ effect does not operate.

But in case of fluoro substituted benzoic acids, a hydrogen bonding should be formed and thus its acidity should decrease.



Just think over it and tax your brain!!



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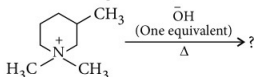
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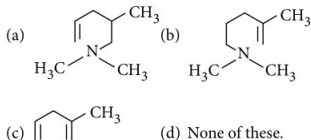
PRACTICE PROBLEMS 2015

Chemistry Olympiad

1. In the following reaction,



the major product is



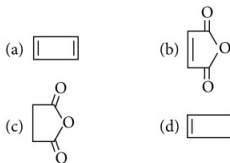
2. A zero-order reaction, $A \longrightarrow \text{Product}$, with an initial concentration $[A]_0$ has a half-life of 0.2 s. If one starts with the concentration $2[A]_0$ then the half-life is
- (a) 0.1 s (b) 0.4 s
(c) 0.2 (d) 0.8 s
3. For the reaction, $X + Y \longrightarrow \text{Products}$, the rate of the reaction increases by a factor of two when the initial concentration of Y is doubled but the rate increases by eight times when the initial concentrations of X and Y are increased by two fold. The rate law for the reaction is
- (a) $\text{rate} = k[X][Y]^2$ (b) $\text{rate} = k[X][Y]$
(c) $\text{rate} = k[X]^2[Y]$ (d) $\text{rate} = k[X]^{1/2}[Y]$
4. The unit cell dimensions of an orthorhombic lattice (with edges a, b, c and the angles between them being α, β, γ)
- (a) $a = b = c, \alpha = \beta = \gamma = 90^\circ$
(b) $a \neq b = c, \alpha = \gamma = 90^\circ, \beta = 90^\circ$
(c) $a = b \neq c, \alpha = \beta = 90^\circ, \gamma \neq 90^\circ$
(d) $a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$

5. Extraction of silver is achieved by initial complexation of the ore (Argentite) with X followed by reduction with Y.

X and Y, respectively, are

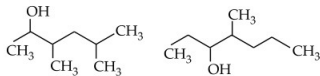
- (a) CN^- and Zn (b) CN^- and Cu
(c) Cl^- and Zn (d) Br^- and Zn

6. A cyclic compound that gives succinic acid on oxidative cleavage is

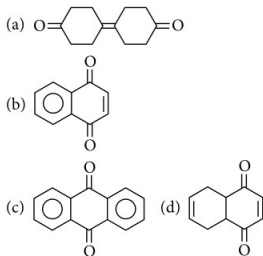


7. The activation energy of a reaction is zero. The rate constant of the reaction
- (a) increases with increase of temperature
(b) decreases with increase of temperature
(c) decreases with decrease of temperature
(d) is nearly independent of temperature.
8. For which one of the following would it not be possible to distinguish high spin from low spin complexes in octahedral geometry?
- (a) Co (II) (b) Fe (II)
(c) Co (III) (d) Ni (II)
9. H_2S would separate the following in pH < 7
- (a) $\text{Ni}^{2+}, \text{Co}^{2+}$ (b) $\text{Cu}^{2+}, \text{Cd}^{2+}$
(c) $\text{Cu}^{2+}, \text{Cr}^{3+}$ (d) $\text{Cu}^{2+}, \text{As}^{3+}$
10. Which base pair has more stability?
- (a) AT (b) CG
(c) AA (d) TT

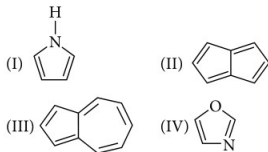
11. The following pairs of compounds are examples of



- (a) chain isomerism only
(b) position isomerism only
(c) both chain and position isomerism
(d) neither chain nor position isomerism
12. Which of the following shows tautomerism?



13. Among



the compound which is not aromatic is

- (a) (I) (b) (II)
(c) (III) (d) (IV)
14. Two solutions having the same vapour pressure are known as
- (a) isopiestic solutions
(b) isotonic solutions
(c) ideal solutions
(d) isodielectric solutions.

15. The presence of potassium ions in solution can be detected by

- (a) Pyroantimonate test
(b) Cobaltinitrite test
(c) Lassaigne's test
(d) Molybdate test.

16. The formation of acetanilide from aniline is an example of

- (a) an aromatic electrophilic substitution
(b) an aromatic nucleophilic substitution
(c) an addition-elimination reaction
(d) a primary amide formation.

17. In both DNA and RNA, heterocyclic base and phosphate ester linkages are at

- (a) C-5' and C-2' respectively of the sugar molecule
(b) C-2' and C-5' respectively of the sugar molecule
(c) C-1' and C-5' respectively of the sugar molecule
(d) C-5' and C-1' respectively of the sugar molecule.

18. At a certain temperature, the first order rate constant k_1 is found to be smaller than the second order rate constant k_2 . If the energy of activation E_1 of the first order reaction is greater than the energy of activation E_2 of the second order reaction, then as the temperature is raised

- (a) k_2 will increase faster than k_1
(b) k_1 will increase faster than k_2 but will always remain less than k_2
(c) k_1 will increase faster than k_2 and become equal to k_2
(d) k_1 will increase faster than k_2 and become greater than k_2 .

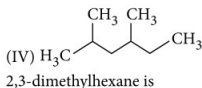
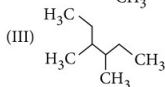
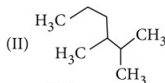
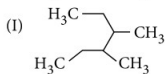
19. Example of isoters are

- (a) CO_2 and SO_2 (b) N_2O and CO_2
(c) NO_2 and SO_2 (d) all of these.

20. An organic compound having molar mass 60 is found to contain C = 20%, H = 6.67% and N = 46.67% while rest is oxygen. On heating, it gives NH_3 along with a solid residue. The solid residue gives violet colour with alkaline CuSO_4 solution. The compound is

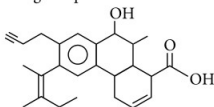
- (a) CH_3CONH_2 (b) $\text{CH}_3\text{CH}_2\text{CONH}_2$
(c) CH_3NCO (d) $(\text{NH}_2)_2\text{CO}$

21. Among the following compounds



- 2,3-dimethylhexane is
(a) (I) (b) (II)
(c) (III) (d) (IV)

22. How many degrees of unsaturation are there in the following compound?



- (a) 6 (b) 7
(c) 10 (d) 11

23. 'Vortex rings' is the

- (a) white smoke of P_2O_5 formed on combustion of phosphine in air
(b) white smoke formed on burning of P in air
(c) white fumes formed due to hydrolysis of PCl_3
(d) none of the above.

24. CaO and NaCl have the same crystal structures and approximately the same ionic radii. If U is the lattice energy of NaCl, the approximate lattice energy of CaO is

- (a) U (b) $2U$
(c) $U/2$ (d) $4U$

25. In a face centred cubic lattice, atom A occupies the corner positions and atom B occupies the face centre positions. If one atom of B is missing from one of the face centred points, the formula of the compound is

- (a) A_2B (b) AB_2
(c) A_2B_3 (d) A_2B_5

26. In pyrophosphoric acid, $\text{H}_4\text{P}_2\text{O}_7$, number of σ - and π - π bonds, respectively, are

- (a) 8 and 2 (b) 6 and 2
(c) 12 and zero (d) 12 and 2

27. In the structure of borax, the numbers of boron atoms and B-O-B units, respectively, are

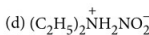
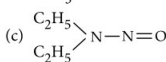
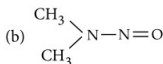
- (a) 4 and 5 (b) 4 and 3
(c) 5 and 4 (d) 5 and 3

28. The decreasing order of reactivity of Chlorobenzene(I), 3-chloronitrobenzene (II), 2-chloronitrobenzene (III) and 4-chlorotoluene (IV) towards aqueous NaOH will be

- (a) $\text{IV} > \text{II} > \text{III} > \text{I}$ (b) $\text{III} > \text{II} > \text{I} > \text{IV}$
(c) $\text{I} > \text{III} > \text{II} > \text{IV}$ (d) $\text{IV} > \text{I} > \text{II} > \text{III}$

29. Diethylamine reacts with HNO_2 to give yellow oily compound due to

- (a) isopropyl alcohol



30. A compound which does not give a positive Lassaigne's test for nitrogen is

- (a) urea (b) glycine
(c) hydrazine (d) pyridine

ANSWER KEY

1. (a) 2. (b) 3. (c) 4. (d) 5. (a)
6. (d) 7. (d) 8. (d) 9. (c) 10. (b)
11. (c) 12. (d) 13. (b) 14. (a) 15. (b)
16. (c) 17. (c) 18. (b) 19. (b) 20. (d)
21. (b) 22. (d) 23. (a) 24. (d) 25. (d)
26. (d) 27. (a) 28. (b) 29. (c) 30. (c)



CROSSWORD

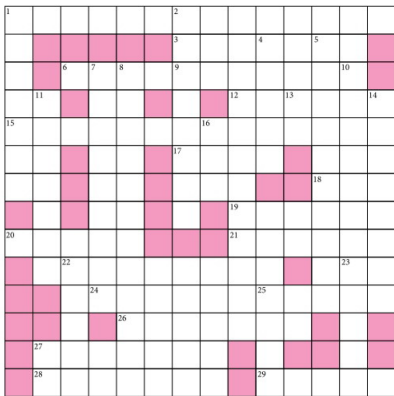
Readers can send their answer to win exciting prizes. Winners' name with their valuable feedback will be published in next issue.

ACROSS

1. A good hydrogenation catalyst. (6)
2. The very reactive element isolated by Moissan. (8)
3. Region, where the probability of finding an electron is maximum. (7)
6. Type of chromatography used to separate sugars and amino acids. (5)
9. An abbreviated form of oxidation-reduction. (5)
13. A furnace for heating chalk to form lime and CO_2 . (4)
15. Compounds having general formula, XX'_n ($n = 1, 3, 5, 7$). (12)
17. Pair of electrons, which do not take part in bonding. (4)
19. A prefix denoting eight. (4)
20. Number of outermost electrons in selenium atom. (3)
21. Pretty lights. (4)
22. An outside agent that affects the speed of a reaction. (8)
24. The first step of esterification. (11)
26. Highly vulcanized rubber containing 20-30% sulphur. (7)
27. A disease caused by deficiency of sunshine vitamin. (7)
28. Measure of molecular disorders. (7)
29. Elements, with lustre property. (5)

DOWN

1. On acid hydrolysis gives a carboxylic acid and an ammonium salt. (7)
2. 37-50% formaldehyde by weight. (8)
4. A charged particle. (3)



5. I'm a functional group present in chocolates. (5)
7. A by-product of lipid metabolism. (7)
8. Technical name of Sodium aluminosilicate. (8)
10. Scientist, who prepared an acid by heating common salt with conc. H_2SO_4 . (7)
11. Reduce acidity. (7)
12. Instantaneous dipole-induced dipole interactions. (6)
14. Nature of N_2O . (7)
16. Yield obtained when the Contact process is operated at low pressure. (3)
18. Impure silicon dioxide. (4)
22. Isomerism, due to the difference in the arrangement of C-atoms. (5)
23. A sugar, the *d*-form of xylose. (4)
25. The smallest unit of an element. (4)

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UNIT-3

Redox Reactions and Electrochemistry | Chemical Kinetics | Surface Chemistry

REDOX REACTIONS AND ELECTROCHEMISTRY

- Redox Reactions
- Balancing of Redox Reactions
- Electrolytic and Metallic Conduction
- Kohlrausch's Law and its Applications
- Electrochemical Cells
- EMF
- Nernst Equation and its Applications
- Relation between Cell Potential and Gibbs Energy
- Dry Cell, Lead Accumulator and Fuel Cells
- Oxidation Number
- Electrode Potential

TIPS TO REMEMBER

Redox Reactions

- These are the reactions which involve oxidation and reduction simultaneously.

Oxidation	Reduction
Addition of oxygen	Removal of oxygen
Removal of hydrogen	Addition of hydrogen
Addition of an electronegative element	Removal of an electronegative element
Removal of an electropositive element	Addition of an electropositive element
Loss of electrons	Gain of electrons
Increase in oxidation number	Decrease in oxidation number

Oxidising and reducing agents :

- A substance which gains electrons or undergoes reduction is known as **oxidising agent**.
- A substance which loses electrons or undergoes oxidation is known as **reducing agent**.

Oxidation Number

- It is defined as the charge which an atom appears to have when all other atoms are removed from it as ions.
- Rules for assigning oxidation number :

Rules	Oxidation number	Examples
Elements	Zero (0)	N_2, Cl_2, O_2, P_4, S_8
Monatomic ions	Same as charge	$Na^+(+1), Mg^{2+}(+2), Cl^-(-1)$
Hydrogen :		
- with non-metals	+1	H_2O, H_2S, HCl
- with metals	-1	LiH, CaH_2, KH
Oxygen :		
- in peroxides	-2 (mostly)	$H_2O, CaO, NaOH$
- in superoxides	-1	H_2O_2, BaO_2
- in fluorides	-1/2	KO_2, CsO_2
	+1, +2	O_2F_2, OF_2 (respectively)
Alkali metals	+1	$Li, Na, K, etc.$

Alkaline earth metals	+2	Be, Mg, Ca, etc.
Fluorine (most electronegative)	-1 (always)	HF, OF ₂ , LiF
Sulphides	-2	H ₂ S, ZnS
<i>p</i> -, <i>d</i> - and <i>f</i> -block elements	Variable	<i>d</i> -block : Fe(+2, +3), Cu(+1, +2), Mn(+7, +6, +5, +4, +3, +2, +1) etc. <i>p</i> -block : As (+3, +5), Sb (+3, +5), Sn (+2, +4), etc. <i>f</i> -block : Ce (+3, +4), Eu (+2, +3)

Balancing of Redox Reactions

□ Oxidation number method :

- Write the skeleton equation representing the chemical change.
- Assign oxidation numbers to the atoms in the equation and find out which atoms are undergoing oxidation and reduction.
- Find the change in oxidation number in each equation.

- Balance those substances which have undergone change in oxidation number and then other atoms except hydrogen and oxygen. Balance hydrogen and oxygen by putting H₂O molecules wherever needed.
- In ionic equations, the net charges on both sides of the equation must be exactly the same. Use H⁺ ion/ions in acidic reactions and OH⁻ ion/ions in basic reactions to balance the charge and number of hydrogen and oxygen atoms.

□ Half reaction method :

- Produce unbalanced equation for the reaction in ionic form.
- Separate the equation into half reactions.
- Balance the atoms other than O and H in each half reaction individually.
- For reactions occurring in acidic medium, add H₂O to balance O atoms and H⁺ to balance H atoms.
- Add electrons to one side of the half reaction to balance the charges. If needed, make the number of electrons equal in the two half reactions by multiplying one or both half reactions by appropriate coefficients.
- Add the two half reactions to achieve the overall reaction and cancel the electrons on each side. This gives the net ionic equation.

Electrolytic and Metallic Conduction

□ Difference between metallic conductors and electrolytic conductors :

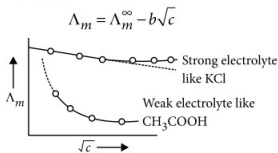
S. No.	Metallic conductors	Electrolytic conductors
1.	Flow of electricity takes place without decomposition of substance.	Flow of electricity takes place with decomposition of substance.
2.	Electricity produced due to movement of electrons (no flow of matter).	Electricity produced due to movement of ions (flow of matter).
3.	As temperature increases, conductance decreases due to increase in kernel vibrations which causes increase in resistance.	As temperature increases, conductance increases due to increase in dissociation.
4.	Resistance caused by vibrating kernels.	Resistance caused by inter-ionic interactions and viscosity of solvent.
5.	Faraday's law is not followed.	Faraday's law is followed.

❑ **Specific, equivalent and molar conductance :**

Property	Specific conductance	Equivalent conductance	Molar conductance
Definition	Reciprocal of specific resistance or conductance of solution of 1 cm length and 1 cm ² area of cross-section	Conductance produced by all the ions of 1 g equivalent electrolyte in a given solution	Conduction produced by all the ions of 1 mol electrolyte in a given solution
Representation	κ (kappa)	Λ_{eq} (lambda)	Λ_m (lambda)
Formula	$\kappa = \frac{1}{\rho} = \frac{l}{Ra} = G \frac{l}{a}$	$\Lambda_{eq} = \kappa \times V = \kappa \times \frac{1000}{\text{Normality}}$	$\Lambda_m = \kappa \times V = \kappa \times \frac{1000}{\text{Molarity}}$
Units	ohm ⁻¹ cm ⁻¹	ohm ⁻¹ cm ² eq ⁻¹	ohm ⁻¹ cm ² mol ⁻¹
SI units	S m ⁻¹	S m ² eq ⁻¹	S m ² mol ⁻¹

❑ **Effect of dilution on conductance :**

- The conductance of solution increases on dilution as larger number of ions are produced.
- The specific conductance decreases on dilution as number of ions present per cm³ of the solution decreases.
- The equivalent and molar conductance increase with dilution.
- The equivalent and molar conductivities tend to acquire maximum value with increasing dilution (maximum at infinite dilution) due to large increase in volume of solution containing 1 gram equivalent or one gram molecule of the electrolyte.
- *Variation of molar conductance with concentration :*
 - For a strong electrolyte it is shown by Debye—Huckel Onsager equation as follows :



Here, Λ_m^∞ = Molar conductance at infinite dilution (Limiting molar conductance)

Λ_m = Molar conductance at V-dilution

b = Constant which depends upon nature of solvent and temperature

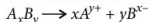
c = Concentration

Kohlrausch's Law

- ❑ The molar conductance of an electrolyte at infinite dilution is the sum of the molar conductances of cations and anions.

$$\Lambda_m^\infty = \lambda_{+}^\infty + \lambda_{-}^\infty$$

λ_{+}^∞ and λ_{-}^∞ are called ionic conductances of cation and anion at infinite dilution respectively.



$$\Lambda_m^\infty = x\lambda_{A^{y+}}^\infty + y\lambda_{B^{x-}}^\infty$$

❑ **Applications of Kohlrausch's law :**

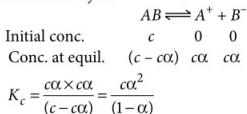
- *Calculation of molar conductance of weak electrolytes :*

$$\begin{aligned} \Lambda_m^\infty \text{CH}_3\text{COOH} &= \lambda_{\text{CH}_3\text{COO}^-}^\infty + \lambda_{\text{H}^+}^\infty \\ &= \left(\lambda_{\text{H}^+}^\infty + \lambda_{\text{Cl}^-}^\infty \right) + \left(\lambda_{\text{CH}_3\text{COO}^-}^\infty + \lambda_{\text{Na}^+}^\infty \right) - \left(\lambda_{\text{Na}^+}^\infty + \lambda_{\text{Cl}^-}^\infty \right) \\ &= \Lambda_m^\infty \text{HCl} + \Lambda_m^\infty \text{CH}_3\text{COONa} - \Lambda_m^\infty \text{NaCl} \end{aligned}$$

- *Calculation of degree of dissociation :*

$$\begin{aligned} \text{Degree of dissociation } (\alpha) &= \frac{\Lambda_m^c}{\Lambda_m^\infty} \\ &= \frac{\text{Conductance at concentration } c}{\text{Conductance at infinite dilution}} \end{aligned}$$

- Calculation of dissociation constant (K_c) of weak electrolyte :



- Determination of ionic product of water :

$$\Lambda^\circ_{H_2O} = \lambda^\circ_{H^+} + \lambda^\circ_{OH^-}$$

$$\Lambda^\circ_{H_2O} = \kappa \times \frac{1000}{\text{Molarity}}$$

$$\text{Molarity} = [H^+] = [OH^-] = \frac{\kappa \times 1000}{\Lambda^\circ_{H_2O}}$$

$$= \frac{\kappa \times 1000}{\lambda^\circ_{H^+} + \lambda^\circ_{OH^-}} = 1.01 \times 10^{-7} \text{ g ions L}^{-1}$$

$$\left[\begin{array}{l} \therefore \lambda^\circ_{H^+} = 349.8 \text{ S cm}^2 \text{ mol}^{-1}, \\ \lambda^\circ_{OH^-} = 198.5 \text{ S cm}^2 \text{ mol}^{-1} \end{array} \right]$$

$$\text{Ionic product of water } (K_w) = [H^+][OH^-] = 1.02 \times 10^{-14}$$

- Determination of solubility of a sparingly soluble salt :

$$\Lambda^\circ_m = \frac{\kappa \times 1000}{\text{Molarity}} = \frac{\kappa \times 1000}{\text{Solubility}}$$

$$\text{Solubility} = \frac{\kappa \times 1000}{\lambda^\circ_+ + \lambda^\circ_-}$$

- Determination of transport number :

$$t^\circ_{\pm} = \frac{\lambda^\circ_{\pm}}{\Lambda^\circ_m} = \frac{\lambda^\circ_{\pm}}{\lambda^\circ_+ + \lambda^\circ_-}$$

t°_+ = Transport number of cation

t°_- = Transport number of anion

Electrochemical Cells

- It is a device which converts chemical energy into electrical energy involving a spontaneous redox reaction.

There are two types of electrochemical cells:

- **Galvanic cell:** In it a spontaneous chemical reaction occurs that generates a voltage.
- **Electrolytic cell:** In it a non-spontaneous chemical reaction is driven by an applied current.

	Galvanic cell	Electrolytic cell
Anode	Oxidation, negative (-) terminal	Oxidation, positive (+) terminal
Cathode	Reduction, positive (+) terminal	Reduction, negative (-) terminal

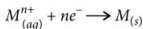
- **Electrode Potential :** It is defined as the tendency of an electrode to gain or lose electrons when it is in contact with the solution of its own ions.
- **EMF:** The electrode potential difference between the two half-cells is known as electromotive force (EMF) of the cell or cell potential or cell voltage.
- It can be calculated from the values of electrode potentials of the two half-cells constituting the cell by using following methods :
 - $E^\circ_{\text{cell}} = E^\circ_{\text{ox}} (\text{anode}) + E^\circ_{\text{red}} (\text{cathode})$
 - When only reduction potential is taken into account,

$$E^\circ_{\text{cell}} = E^\circ_{\text{red}} (\text{cathode}) - E^\circ_{\text{red}} (\text{anode})$$

$$= E^\circ_{\text{right}} - E^\circ_{\text{left}}$$
 - When only oxidation potential is taken into account,

$$E^\circ_{\text{cell}} = E^\circ_{\text{ox}} (\text{anode}) - E^\circ_{\text{ox}} (\text{cathode})$$

Nernst Equation



$$E = E^\circ - \frac{RT}{nF} \ln \frac{[M_{(s)}]}{[M^{n+}_{(aq)}]}$$

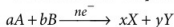
For pure solid or liquid or gas at 1 atm pressure, the molar concentration is taken as unity; $[M] = 1$

$$E = E^\circ - \frac{2.303RT}{nF} \log \frac{1}{[M^{n+}_{(aq)}]}$$

$$E = E^\circ - \frac{0.0591}{n} \log \frac{1}{[M^{n+}_{(aq)}]}$$

- **Applications of Nernst equation :**

- To calculate electrode potential of a cell :



$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log \frac{[X]^x [Y]^y}{[A]^a [B]^b}$$

- To calculate equilibrium constant :

At equilibrium, $E_{\text{cell}} = 0$

$$E_{\text{cell}}^{\circ} = \frac{0.0591}{n} \log K_c \text{ at } 298 \text{ K}$$

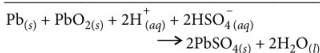
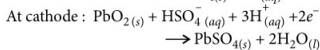
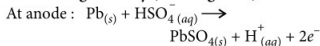
□ Relation between Cell Potential and Gibbs Energy

$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$$

$$\Delta G^{\circ} = -2.303 RT \log K_c$$

Dry Cell, Lead Accumulator and Fuel Cells

□ Lead storage battery (Rechargeable) :



□ Dry cell

- Common dry cell battery (Non-rechargeable) :

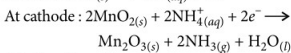
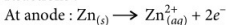
- Leclanche cell :

Anode : Zinc container

Cathode : Graphite rod surrounded by paste of MnO_2 and carbon black.

Electrolyte : Moist paste of NH_4Cl and ZnCl_2 in starch.

Reactions :

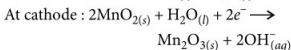
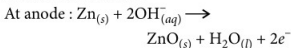


- Alkaline dry cell :

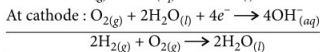
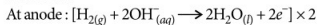
- Modified version of Leclanche cell.

- NH_4Cl is replaced with KOH or NaOH .

- Alkaline cells last longer than Leclanche cells because zinc corrodes more slowly in a basic environment.



□ Fuel cell :



Key Points

- Faraday's law of electrolysis :

- Faraday's first law of electrolysis

$$w = Z \times I \times t$$

- Faraday's second law of electrolysis

$$\frac{\text{wt. of X deposited}}{\text{wt. of Y deposited}} = \frac{\text{Eq. wt. of X}}{\text{Eq. wt. of Y}}$$

- Substances with stronger reducing power are placed above hydrogen and those with weaker reducing power are placed below hydrogen in an electrochemical series.

- While applying Nernst equation electrode potential is always taken as reduction potential.

CHEMICAL KINETICS

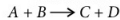
- Rate of Chemical Reaction
- Factors Affecting Rate of Reaction
- Elementary and Complex Reactions
- Order and Molecularity of Reaction
- Methods of Determining Order of Reaction
- Rate Law and Rate Constant
- Half-life of Reaction
- Activation Energy
- Arrhenius Theory
- Collision Theory

TIPS TO REMEMBER

Rate of Chemical Reaction

- The rate of reaction is the change in the concentration of any one of the reactants or products per unit time.

$$\text{Rate} = \frac{\text{Decrease in conc. of reactant}}{\text{Time taken}} = \frac{\text{Increase in conc. of product}}{\text{Time taken}}$$



$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{\Delta[B]}{\Delta t} = +\frac{\Delta[C]}{\Delta t} = +\frac{\Delta[D]}{\Delta t}$$

Negative sign shows decrease in concentration with time and positive sign shows increase in concentration with time.

□ Units :

$$\text{Rate} = \frac{\text{Concentration}}{\text{Time}} = \frac{\text{mol/litre}}{\text{sec}} = \text{mol litre}^{-1} \text{sec}^{-1}$$

Factors Affecting Rate of Reaction

□ Nature of reactants and products :

- *Physical state* :

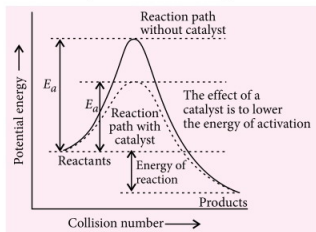
Gaseous state > Liquid state > Solid state

Decreasing rate of reaction →

- *Size of reactants* : As size of reactant decreases, rate of reaction increases. Rate of reaction is maximum in powdered state because of increase in surface area.
- *Chemical nature* : Rate of reaction increases if the number of bonds broken and formed in the reactions are lesser in number.
- *Concentration of reactants* : Rate of the reaction is directly proportional to concentration of the reactant.

□ **Temperature** : Rate of reaction increases considerably with an increase in temperature.

□ **Catalyst** : A positive catalyst increases the reaction rate by changing the path of reaction and lowering the activation energy.



□ **Surface area** : Larger the surface area of the reactants, faster is the rate of reaction.

□ **Exposure to radiation** : The rate of chemical reaction is considerably increased by the use of radiations of certain frequency.

Elementary and Complex Reactions

- Reactions which get completed only in one step are called elementary reactions.
- Reactions which involve more than one step for completion of reaction are called complex reactions.

Order and Molecularity of Reaction

Molecularity of reaction	Order of reaction
It is the total number of species taking part in a chemical reaction.	It is the sum of the powers of the concentration terms of the reacting species in rate law.
It is a theoretical concept.	It is an experimental quantity.
It is derived from the mechanism of reaction.	It is derived from the rate expression.
It can neither be zero nor fractional. It is always a whole number.	It may be zero, fractional or an integer (may range from 0 to 3).
It is applicable only to elementary reactions. The overall molecularity of a complex reaction has no significance.	It is applicable to elementary as well as complex reactions.

Methods of Determining Order of Reaction

□ **Method of integration (Hit and Trial method)**: It involves the substitution of experimental values of a and x at a given time, in different rate equations.

- For zero order reaction, $k = \frac{x}{t}$

- For first order reaction,

$$k = \frac{2.303}{t} \log \frac{a}{(a-x)}$$

- For second order reaction,

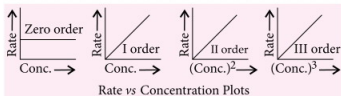
$$k = \frac{1}{t} \left[\frac{1}{(a-x)} - \frac{1}{a} \right]$$

- For third order reaction,

$$k = \frac{1}{2t} \left[\frac{1}{(a-x)^2} - \frac{1}{a^2} \right]$$

□ **Graphical method** : It involves determining the rate for a given change at different concentrations of reactants.

- Graphs are then plotted between rates and concentrations, the nature of which suggest the order.

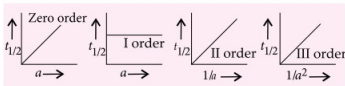


- **Fractional change method (Half-life method):**
It involves conducting the reaction at different concentrations and determining time required to complete a definite fraction.

It involves the use of the general expression for the half-life and plotting the half-life ($t_{1/2}$) vs concentration (a^{1-n}).

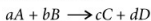
$$t_{1/2} \propto \frac{1}{a^{n-1}}$$

- For zero order reaction, $t_{1/2} \propto a$
- For first order reaction, $t_{1/2}$ is independent of a , i.e. $t_{1/2} = \text{constant}$.
- For second order reaction, $t_{1/2} \propto 1/a$, i.e. $t_{1/2} a = \text{constant}$.
- For third order reaction, $t_{1/2} \propto \frac{1}{a^2}$, i.e. $t_{1/2} a^2 = \text{constant}$
- For n^{th} order reaction, $t_{1/2} \propto \frac{1}{a^{n-1}}$, i.e. $t_{1/2} a^{n-1} = \text{constant}$



Rate Law and Rate Constant (Law of Mass Action)

- The rate of reaction is proportional to the product of effective concentrations of the reacting species, each raised to a power which is equal to the corresponding stoichiometric number of the molecules appearing in the chemical reaction.



$$r \propto [A]^a [B]^b \quad \text{or} \quad r = k[A]^a [B]^b$$

k is the constant of proportionality.

Rate of reaction at unit concentration of reactants is called rate constant.

- **Units of rate constant :**

$$k = \frac{r}{[A]^a [B]^b}$$

$$= \frac{\text{Concentration}}{\text{Time}} \times \frac{1}{(\text{Concentration})^n}$$

SI unit of concentration is mol L^{-1} and that of time is s.

Half-Life of Reaction ($t_{1/2}$)

- It is the time in which the concentration of a reactant is reduced to one-half of its initial concentration.

$$t_{1/2} \propto \frac{1}{a^{n-1}}$$

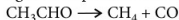
where, n is the order of the reaction.

Rate Law, Integrated Rate Law, Half-Life, Unit of Rate Constant and Graph for the Reactions of Different Orders

Order	Rate law	Integrated rate law	Half-life	Unit of rate constant	Graph
0	$\text{Rate} = k[A]^0$	$[A]_t = -kt + [A]_0$	$t_{1/2} = [A]_0/2k$	$\text{mol L}^{-1} \text{ s}^{-1}$	$[A]$ vs t ; slope = $-k$
1	$\text{Rate} = k[A]^1$	$\ln[A]_t = -kt + \ln[A]_0$	$t_{1/2} = 0.693/k$	s^{-1}	$\ln[A]$ vs t ; slope = $-k$
2	$\text{Rate} = k[A]^2$	$1/[A]_t = kt + 1/[A]_0$	$t_{1/2} = 1/k[A]_0$	$\text{L mol}^{-1} \text{ s}^{-1}$	$1/[A]$ vs t ; slope = k
2	$\text{Rate} = k[A][B]$	$kt = \frac{1}{[A]_0 - [B]_0} \ln \frac{[B]_0[A]}{[A]_0[B]}$	$t_{1/2} = 1/k[A]_0$	$\text{L mol}^{-1} \text{ s}^{-1}$	$1/[A]$ vs t ; slope = k
n	$\text{Rate} = k[A]^n$	$(n-1)kt = \frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}}$	$t_{1/2} = \frac{2^{n-1} - 1}{k(n-1)[A]_0^{n-1}}$	$(\text{mol L}^{-1})^{1-n} \text{ s}^{-1}$	$\frac{1}{[A]^{n-1}}$ vs t ; slope = k

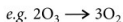
- ❑ **Fractional order reaction** : There are some reactions for which order of reaction is not an integer.

e.g., Decomposition of CH_3CHO



$$\text{Rate} = k[\text{CH}_3\text{CHO}]^{3/2}$$

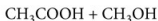
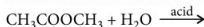
- ❑ **Negative order reaction** : In negative order reaction, rate of reaction decreases as the concentration of one of the constituent increases.



$$\text{Rate} = k[\text{O}_3]^2[\text{O}_2]^{-1}$$

Therefore, the order of reaction with respect to oxygen is -1 .

- ❑ **Pseudounimolecular Reaction** :

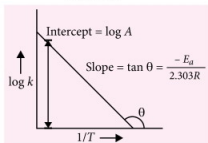


According to law of mass action, given reaction should be bimolecular, but as water is present in large excess, its concentration remains practically constant, so, does not affect the rate of reaction.

Arrhenius Theory

- ❑ **Arrhenius equation** : $k = Ae^{-E_a/RT}$

$$\log k = \log A - \frac{E_a}{2.303 RT}$$



where k = Rate constant,

A = Pre-exponential factor (frequency factor),

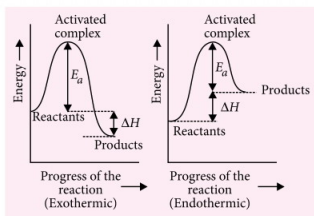
E_a = Activation energy,

T = Temperature

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Activation Energy

- ❑ The minimum amount of energy required by reactant molecules to participate in a reaction is called **activation energy**.



- Activation energy = Threshold energy – Average kinetic energy of reacting molecules
- Threshold energy
= Initial potential energy of reactant molecules + Activation energy
- Activation energy (E_a)
= $E_{(\text{activated complex})} - E_{(\text{ground state})}$
- ΔH = Activation energy of forward reaction – Activation energy of backward reaction

Collision Theory

- ❑ Reactions occur when molecules collide with appropriate orientation and sufficient energy, not all molecular collisions result successfully in the formation of product.
- ❑ **For any successful collision** :
 - particles must collide.
 - they must collide with sufficient energy $> E_a$.
 - they need to have correct alignment (collision geometry) to keep E_a as low as possible.
- ❑ To account for effective collision, another factor P , called orientation factor or steric factor or probability factor is introduced.

$$k = PZ_{AB} e^{-E_a/RT}$$
 where, Z_{AB} represents the collision frequency of reactants A and B .
Thus, in collision theory, activation energy and proper orientation of the molecules determine the criteria for an effective collision and hence the rate of reaction.

Key Points

- $T = n \times t_{1/2}$
where, T = Total time, n = Number of half-lives.
Amount of substance left after ' n ' half-lives $[A] = \frac{[A]_0}{2^n}$
- For a first order reaction,
 $T_{75} = 2 \times T_{50}$, $T_{87.5} = 3 \times T_{50}$,
 $T_{99.9} = 10 \times T_{50}$
- Temperature coefficient $= \frac{k_{T+10}}{k_T} \approx 2-3$

SURFACE CHEMISTRY

- Adsorption
- Catalysis
- Colloidal state
- Emulsions

TIPS TO REMEMBER

Adsorption

□ Terminology

S.No.	Terms	Definition
1.	Absorption	Phenomenon in which the particles of gas or liquid get uniformly distributed throughout the body of the solid.
2.	Adsorption	Phenomenon of attracting the molecules of a substance on the surface of a liquid or solid, resulting in a higher concentration of molecules on the surface.
3.	Adsorbate	Substance being adsorbed.
4.	Adsorbent	Substance on whose surface, adsorbate is being adsorbed.
5.	Sorption	When both adsorption and absorption occur simultaneously.
6.	Desorption	Reverse adsorption <i>i.e.</i> , removal of the adsorbed substance from the surface of the adsorbent.
7.	Occlusion	Adsorption of gases on a metal surface.

8.	Enthalpy of adsorption	Enthalpy change accompanying the adsorption of 1 mole of adsorbate on the adsorbent surface.
9.	Adsorption isotherm	A graph between extent of adsorption and pressure of the gas at constant temperature.
10.	Physical adsorption	Process in which adsorbate particles are held on the surface of adsorbent by weak van der Waals' forces.
11.	Chemical adsorption	Process in which adsorbate molecules are held on the surface of adsorbent by chemical forces.
12.	Positive adsorption	Occurs when concentration of adsorbate is more on surface of the adsorbent than in the bulk.
13.	Negative adsorption	Occurs when concentration of adsorbate on the surface of the adsorbent is less than that in the bulk.

□ Comparison of physisorption and Chemisorption :

S.No.	Physisorption	Chemisorption
1.	It arises because of van der Waals' forces.	It is caused by chemical bond formation.
2.	It is not specific in nature.	It is highly specific in nature.
3.	It is reversible.	It is irreversible.
4.	It depends on the nature of the gas. More easily liquefiable gases are adsorbed readily.	It also depends on the nature of the gas. Gases which can react with the adsorbent show chemisorption.
5.	Enthalpy of adsorption is low (20 - 40 kJ mol ⁻¹).	Enthalpy of adsorption is high (80 - 240 kJ mol ⁻¹).

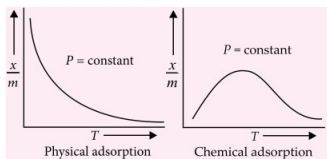
6.	Low temperature is favourable for adsorption. It decreases with increase of temperature.	High temperature is favourable for adsorption. It increases with the increase of temperature.
7.	No appreciable activation energy is needed.	High activation energy is sometimes needed.
8.	It depends on the surface area. It increases with increase in surface area of adsorbent.	It also depends on the surface area and increases with increase in surface area of adsorbent.
9.	It results into multimolecular layers on adsorbent surface under high pressure.	It results into unimolecular layer.

❑ **Factors affecting adsorption of gases on solids :**

- **Nature of adsorbate (gas) :** More readily soluble and easily liquefiable gases are adsorbed more easily than the permanent gases. The ease of liquefaction of gas depends on its critical temperature. Higher the T_C , more easily it will liquefy.
- **Nature of adsorbent (solid) :** The substance which is highly porous or finely divided, will have large adsorption power. Most common adsorbents are activated carbon, silica gel, aluminium oxide and clay.
- **Surface area of solid :** The surface area per gram of the adsorbent is called specific area. Larger is the specific area of solid, greater will be the adsorbing capacity.
- **Temperature :** Adsorption is an exothermic process therefore as temperature increases, adsorption decreases. But chemisorption first increases with temperature and after a particular extent, decreases with increase in temperature.
- **Pressure :** At constant temperature, the adsorption of a gas increases with increase in pressure.

❑ **Adsorption Isobars**

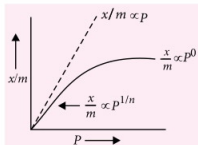
- A graph between extent of adsorption (x/m) and temperature (T) at a constant pressure of adsorbate gas is known as adsorption isobars.



❑ **Adsorption Isotherms**

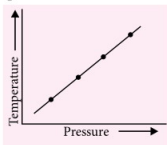
Adsorption Isotherms	
Freundlich adsorption isotherm	Langmuir adsorption isotherm
Relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature.	On the basis of kinetic theory, Langmuir derived an expression for adsorption isotherm.
$\frac{x}{m} = k \cdot P^{1/n} (n > 1)$	$\frac{P}{(x/m)} = \frac{1}{k'} + \left(\frac{k}{k'}\right)P$
$\log \frac{x}{m} = \log k + \frac{1}{n} \log P$	$\frac{x}{m} = \frac{k'P}{1 + kP}$
The factor $1/n$ can have values between 0 and 1.	When pressure is very high then $1 + kP \approx kP$ $\Rightarrow \frac{x}{m} = \frac{k'P}{kP} = \text{constant}$
When $1/n = 0$, $x/m = \text{constant}$ which shows that adsorption is independent of pressure.	When pressure is very high then $1 + kP \approx 1$ $\Rightarrow x/m = k'P$
When $1/n = 1$, $x/m = kP$, the adsorption varies directly with pressure.	When pressure is moderate then $x/m = kP^{1/n}$, $1/n$ lies between 0 and 1.

- Freundlich equation does not apply to adsorption of gases at higher pressure.



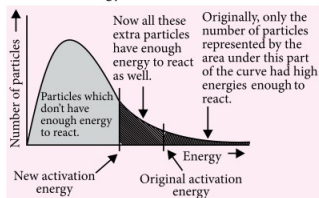
Adsorption isostere

- The plot of temperature vs pressure for a given amount of adsorption is called adsorption isostere.



Catalysis

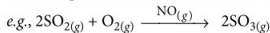
- A substance which influences the rate of reaction without being consumed in the reaction is called **catalyst** and the phenomenon is called **catalysis**. Catalyst causes decrease in activation energy.



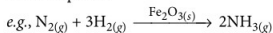
Catalyst

- Positive catalyst** : Increases the rate of reaction.
- Negative catalyst** : Decreases the rate of reaction.
- Auto catalyst** : One of the products acts as catalyst.
- Induced catalyst** : One reaction influences the rate of other reaction which does not occur under ordinary conditions.

- Homogeneous catalyst** : Catalyst that is in the same phase as the reaction mixture.



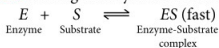
- Heterogeneous catalyst** : Catalyst is in a different phase.



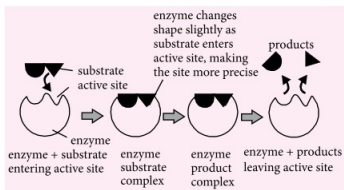
- Enzyme catalysis** : Enzymes are biological catalysts produced by living cells which catalyse the biochemical reactions in living organisms. Chemically all enzymes are proteins.

- Enzyme catalysis mechanism** : Enzyme catalysed reactions are highly specific.

Step 1 : Binding of enzyme with substrate.



Step 2 : Dissociation of ES complex.



Colloidal State

- Suspension, colloid and true solution** :

Suspension	Colloid	True solution
Size : $> 10^{-5}$ cm	10^{-7} to 10^{-5} cm	$< 10^{-7}$ cm
Visible with naked eyes	Visible with ultramicroscope	Not visible by any optical means
Does not diffuse	Diffuses very slowly	Diffuses rapidly
Settles under gravity	Does not settle but it may settle under centrifuge	Does not settle
Heterogeneous	Heterogeneous	Homogeneous
Opaque	Generally clear	Clear

❑ **Classification of colloids :**

A. Depending on the physical states of dispersed phase and dispersion medium :

Dispersed phase	Dispersion medium	Name	Common examples
Gas	Gas	One phase system	
	Liquid	Foam	Soap, whipped cream
	Solid	Solid foam	Pumice stone, styrene rubber
Liquid	Gas	Aerosol	Fog, clouds, mist
	Liquid	Emulsion	Milk, emulsified oil
	Solid	Gel	Cheese, butter, boot polish
Solid	Gas	Aerosol	Smoke, volcanic dust
	Liquid	Sol	Paints, ink
	Solid	Solid sol	Ruby, glass, some gemstones

B. Depending on the nature of interaction between dispersed phase and dispersion medium :

- Lyophilic colloids
- Lyophobic colloids

Property	Lyophilic colloids	Lyophobic colloids
Interaction	Strong	Weak
Preparation	By heating or warming	By special methods
Reversibility	Reversible	Irreversible
Stability	More stable	Less stable
Viscosity	Higher than medium	Same as medium

Surface tension	Lower than medium	Same as medium
Action of electrolyte	Not easily precipitated	Coagulation takes place
Hydration	Extensive	No hydration
Examples	Gum, gelatin, starch, protein, rubber, etc.	Solutions of metal like Ag, Au, metal sulphides like As_2S_3 etc.

C. Depending upon the type of particles of dispersed phase :

- Multimolecular colloids
- Macromolecular colloids
- Associated colloids or micelles
- *Multimolecular colloids* : These solutions consist of aggregates of atoms or small molecules with diameter of less than 1 nm and the molecules are held together with van der Waals' forces.
e.g., gold sols, sulphur (S_8) molecules
- *Macromolecular colloids* : In these colloids, the dispersed particles are themselves large molecules (usually polymers). Most lyophilic sols belong to this category.
- *Micelles* : There are certain colloids which behave as normal strong electrolytes at low concentrations, but exhibit colloidal properties at higher concentration due to the formation of aggregated particles. These are known as micelles or associated colloids.

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Preparation of Colloidal Solutions

I. Dispersion method

Mechanical dispersion

Particles are ground to colloidal size and are then dispersed in liquid (performed in colloid mill) e.g., Colloidal graphite and ink

Electro-dispersion

An arc is struck between two metal (dispersed phase) electrodes under the surface of water (medium) containing KOH (stabilizer) e.g., colloidal solutions of metals like Au, Ag, Pt.

Ultrasonic dispersion

Substances like oil, mercury, sulphur, oxides of metals can be dispersed into colloidal state with the help of ultrasonic waves.

Peptization

The dispersion of a freshly precipitated material into colloidal solution by the action of an electrolyte in the solution is termed as peptization and electrolyte used is called a peptizing agent.

II. Condensation method

Exchange of solvents

A number of substances are there whose colloidal solutions can be prepared by taking a solution of the substance in one solvent and pouring it into another solvent in which the substance is less soluble. e.g. Alcoholic solution of sulphur.

By change of physical state

Sols of substances like Hg and sulphur are prepared by passing their vapours through cold water containing a stabilizer such as ammonium salt or citrate.

Chemical methods

Oxidation

Sol of sulphur

Reduction

Sol of Pt, silver, etc.
Gold sol (purple of Cassius).

Double decomposition

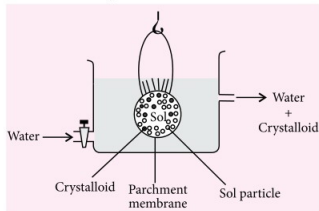
Sol of As_2S_3

Hydrolysis

Sol of $Fe(OH)_3$

Purification of Colloidal Solutions

- ❑ **Dialysis** : It is the process of separating the particles of colloidal dimensions by means of diffusion through a suitable membrane.



- ❑ **Electrodialysis** : In this process, electric field is applied during dialysis.

Properties of Colloidal Solutions

- ❑ **General physical properties** :

- **Heterogeneity** : Colloidal solutions are heterogeneous in nature and consist of two phases—dispersed phase and dispersion medium.
- **Visibility of dispersed particles** : The dispersed particles present in them are not visible to the naked eye and they appear homogeneous. This is because colloidal particles are too small to be visible to the naked eye.

- **Filtrability** : Due to very small size, the colloidal particles pass through an ordinary filter paper. However, they can be retained by animal membranes, cellophane membrane and ultrafilters.
- **Stability** : Lyophilic sols in general and lyophobic sols in the absence of substantial concentrations of electrolytes are quite stable and the dispersed particles present in them do not settle down even on keeping.
- **Colour** : The colour of a colloidal solution depends upon the size of colloidal particles present in it. Larger particles absorb the light of longer wavelength and therefore transmit light of shorter wavelength.

❑ Mechanical properties :

- **Diffusion** : The sol particles diffuse from higher concentration to lower concentration region. However, due to bigger size, they diffuse at a lesser speed.
- **Sedimentation** : The colloidal particles settle down under the influence of gravity at a very slow rate. This phenomenon is used for determining the molecular mass of the macromolecules.
- **Brownian movement** : The colloidal particles move randomly in a zig-zag motion. This type of motion is called Brownian movement. The molecules of the dispersion medium are constantly colliding with the particles of the dispersed phase. The Brownian movement explains the force of gravity acting on colloidal particles. This helps in providing stability to colloidal sols by not allowing them to settle down.

❑ Electrical properties :

- **Electrophoresis** : The phenomenon of movement of colloidal particles under an applied electric field is called electrophoresis. If the particles accumulate near the negative electrode, the charge on the particles is positive. On the other hand, if the sol particles accumulate near the positive electrode, the charge on the particles is negative.

- **Electro-osmosis** : Electro-osmosis is a phenomenon in which dispersion medium is allowed to move under the influence of an electrical field, whereas colloidal particles are not allowed to move.

❑ Charge on colloidal particles :

Positively charged sols	Negatively charged sols
Hydrated metallic oxides. e.g., $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$	Metallic particles. e.g., Cu, Ag, Au
Metal hydroxides, $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$	Metal sulphides. e.g. As_2S_3 , CdS
Basic dyestuffs like Prussian blue.	Acidic dyes like eosin, congo red etc.
Haemoglobin (blood)	Sols of gelatin, gum, starch, etc.

❑ Optical Properties

- **Tyndall effect** : It is scattering of light by colloids.
- **Coagulation or flocculation** : It is the phenomenon of precipitation of a colloidal solution by the addition of an electrolyte.
 - The minimum concentration of an electrolyte required to cause coagulation of one litre of the colloidal sol is called its **flocculation value** and is usually expressed in millimoles per litre.
 - **Hardy—Schulze rule** : The greater the valency of the coagulating ion added, the greater is its power to cause coagulation.

Key Points

- Flocculation value

$$\propto \frac{1}{\text{Coagulating power}}$$
- Number of mg of the dry protective colloid required to just prevent the coagulation of 10 ml of red gold sol when 1 ml of 10% solution of NaCl is added to it, is known as **gold number**.
- Protective power $\propto \frac{1}{\text{Gold number}}$

Emulsions

- Emulsions are the colloidal systems in which both the dispersed phase and dispersion medium are liquids. They are stabilized by addition of substances called emulsifiers or emulsifying agents.

Types of Emulsions

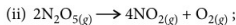
- **Oil in Water (O/W) type** : In this type, oil is dispersed phase and water is the dispersion medium. Milk is an emulsion of O/W type, where fat globules are dispersed in water.
- **Water in Oil (W/O) type** : In this type, water is the dispersed phase and oil is the dispersion medium. Butter is an emulsion of W/O type.

Properties of Emulsions

- Emulsions exhibit all the properties like Tyndall effect, Brownian movement, Electrophoresis, Coagulation on addition of electrolytes as shown by colloidal sols.
- Emulsions can be broken to yield the constituent liquids by heating, centrifuging, by adding larger amounts of the electrolytes to precipitate out the dispersed phase or by chemical destruction of the emulsifying agent. The separation of cream from milk is a well known example of centrifuging.
- The size of the dispersed particles in emulsion is larger than those in the sols. It ranges from 1000 Å to 10000 Å.

Questions for Practice

- The oxidation number of S in $\text{Na}_2\text{S}_4\text{O}_6$ is
 - + 2.5 for each S atom
 - + 2 and + 3 (two S have + 2 and other two have + 3)
 - + 2 and + 3 (three S have + 2 and one S has + 3)
 - + 5 and 0 (two S have + 5 and other two have 0).
- The EMF of a concentration cell consisting of two zinc electrodes, one dipping into $M/4$ solution of ZnSO_4 and the other into $M/16$ solution of the same salt at 25°C is
 - 0.0125 V
 - 0.0250 V
 - 0.0178 V
 - 0.0356 V
- For a reaction, $X \longrightarrow Y$, the graph of the product concentration (x) versus (t) came out to be a straight line passing through the origin. Hence the graph of $\left(\frac{-d[X]}{dt}\right)$ and time would be
 - straight line with a negative slope and an intercept on y -axis
 - straight line with a positive slope and an intercept on y -axis
 - a straight line parallel to x -axis
 - a hyperbola.
- Which of the following can adsorb larger volume of hydrogen gas?
 - Finely divided nickel
 - Colloidal solution of palladium
 - Finely divided platinum
 - Colloidal $\text{Fe}(\text{OH})_3$
- The equivalent weight of Mohr's salt is equal to
 - its molecular weight
 - atomic weight
 - half of its molecular weight
 - one-third of its molecular weight.
- The standard reduction potential of $\text{Cu}^{2+}|\text{Cu}$ and $\text{Ag}^+|\text{Ag}$ electrodes are 0.337 V and 0.799 V, respectively. For what concentration of Ag^+ electrodes, will the emf of the cell be zero at 25°C if the concentration of Cu^{2+} ions is 0.01 M?
 - 1.352×10^{-9} M
 - 1.532×10^{-9} M
 - 1.235×10^{-9} M
 - 1.523×10^{-9} M
- For the first order decomposition reaction of N_2O_5 , it is observed that
 - $\text{N}_2\text{O}_5(\text{g}) \longrightarrow 2\text{NO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$;
$$-\frac{d[\text{N}_2\text{O}_5]}{dt} = k[\text{N}_2\text{O}_5]$$



$$-\frac{d[\text{N}_2\text{O}_5]}{dt} = k'[\text{N}_2\text{O}_5]$$

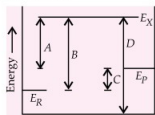
Which of the following is true?

- (a) $k = k'$ (b) $k = 2k'$
 (c) $k = \frac{k'}{2}$ (d) $k = k'^2$
8. The stabilization of the dispersed phase in a lyophobic sol is due to
 (a) liking for the dispersion medium
 (b) the surface tension of the medium
 (c) the formation of an electrical layer between the two phases
 (d) the viscosity of the medium.
9. In which of the following compounds, the oxidation number of iodine is fractional?
 (a) IF_7 (b) I_3^-
 (c) IF_5 (d) IF_3
10. For the redox reaction,
 $\text{Zn} + \text{NO}_3^- \rightarrow \text{Zn}^{2+} + \text{NH}_4^+$ (in basic medium)
 coefficients of Zn , NO_3^- and OH^- in the balanced equation respectively are
 (a) 4, 1, 7 (b) 7, 4, 1
 (c) 4, 1, 10 (d) 1, 4, 10.
11. Which of the following statements is true for a second order reaction?
 (a) $t_{1/2} \propto 1/a$
 (b) unit of k is s^{-1}
 (c) $k = \frac{1}{t} \cdot \frac{a(a-x)}{x}$
 (d) $t_{1/2}$ is independent of initial concentration
12. Butter is a colloid formed when
 (a) fat is dispersed in water
 (b) fat globules are dispersed in water
 (c) water is dispersed in fat
 (d) none of the above.
13. Amount of oxalic acid present in a solution can be determined by its titration with KMnO_4 solution in the presence of H_2SO_4 . The titration gives unsatisfactory result when carried out in the presence of HCl , because HCl

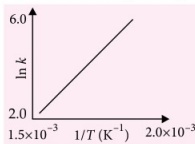
- (a) oxidises oxalic acid to carbon dioxide and water
 (b) gets oxidised by oxalic acid to chlorine
 (c) furnishes H^+ ions in addition to those from oxalic acid
 (d) reduces permanganate to Mn^{2+} .

14. The time required to coat a metal surface of 80 cm^2 with $5 \times 10^{-3} \text{ cm}$ thick layer of silver (density 1.05 g cm^{-3}) with a passage of 3 A current through a silver nitrate solution is
 (a) 115 sec (b) 125 sec
 (c) 135 sec (d) 145 sec
15. The time for half life period of a certain reaction $A \longrightarrow \text{Products}$ is 1 hour. When the initial concentration of the reactant A is 2.0 mol L^{-1} , how much time does it take for its concentration to come from 0.50 to 0.25 mol L^{-1} if it is a zero order reaction?
 (a) 1 h (b) 4 h
 (c) 0.5 h (d) 0.25 h
16. Under the influence of an electric field, the particles in a sol migrate towards cathode. The coagulation of the same sol is studied using NaCl , Na_2SO_4 and Na_3PO_4 solutions. Their coagulating values will be in the order
 (a) $\text{NaCl} > \text{Na}_2\text{SO}_4 > \text{Na}_3\text{PO}_4$
 (b) $\text{Na}_2\text{SO}_4 > \text{Na}_3\text{PO}_4 > \text{NaCl}$
 (c) $\text{Na}_3\text{PO}_4 > \text{Na}_2\text{SO}_4 > \text{NaCl}$
 (d) $\text{Na}_2\text{SO}_4 > \text{NaCl} > \text{Na}_3\text{PO}_4$
17. Oxidation state of Cl in CaOCl_2 is
 (a) 0 (b) +1
 (c) -1 (d) +1, -1
18. A solution containing 4.5 mM of $\text{Cr}_2\text{O}_7^{2-}$ and 15 mM of Cr^{3+} shows a pH of 2.0. Calculate the electrode potential of half reaction.
 (Given : standard potential of reaction
 $\text{Cr}_2\text{O}_7^{2-} \longrightarrow \text{Cr}^{3+}$ is 1.33 V)
 (a) 2.4 V (b) 1.8 V
 (c) 1.07 V (d) 1.10 V

19. In the accompanied diagram, E_R , E_P and E_X represent the energy of the reactants, products and activated complex respectively. Which of the following is the activation energy for the backward reaction?



- (a) A (b) B
(c) C (d) D
20. Which relation represents Freundlich adsorption isotherm?
- (a) $x/m = kP$ at low pressure
(b) $x/m = k$ at high pressure
(c) $\log x/m = \log k + 1/n \log P$
(d) All of the above.
21. MnO_4^{2-} (1 mole) in neutral aqueous medium is disproportionated to
- (a) $2/3$ mole of MnO_4^- and $1/3$ mole of MnO_2
(b) $1/3$ mole of MnO_4^- and $2/3$ mole of MnO_2
(c) $2/3$ mole of MnO_2 and $1/3$ mole of Mn_2O_7
(d) $2/3$ mole of Mn_2O_7 and $1/3$ mole of MnO_2 .
22. A gas X at 1 atm is bubbled through a solution containing a mixture of $1\text{ M } Y^-$ and $1\text{ M } Z^-$ at 25°C . If their reduction potentials are in the order, $Z > Y > X$ then
- (a) Y will oxidize X but not Z
(b) Y will oxidize Z but not X
(c) Y will oxidize both X and Z
(d) Y will reduce both X and Z.
23. A plot of $\ln k$ versus inverse of temperature for reaction is shown in the given figure :

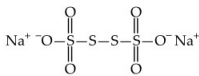


The reaction must be

- (a) exothermic
(b) endothermic
(c) one with negligible enthalpy change
(d) highly spontaneous at ordinary temperature.
24. Tyndall effect in a colloid is due to
- (a) interference of light
(b) diffraction of light
(c) reflection of light
(d) scattering of light.
25. For decolourisation of 1 mole of acidified KMnO_4 , the moles of H_2O_2 required is
- (a) $1/2$ (b) $3/2$
(c) $5/2$ (d) $7/2$
26. Given : $E^\circ_{\text{Fe}^{3+}/\text{Fe}} = -0.036\text{ V}$, $E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.439\text{ V}$. The value of standard electrode potential for the change, $\text{Fe}^{3+}_{(\text{aq})} + e^- \rightarrow \text{Fe}^{2+}_{(\text{aq})}$ will be
- (a) -0.072 V (b) 0.385 V
(c) 0.77 V (d) -0.27 V
27. The half-life of first order decomposition of NH_2NO_2 is 2.10 hr at 288 K temperature.
 $\text{NH}_2\text{NO}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$
If 6.2 g of NH_2NO_2 is allowed to decompose, the time required for NH_2NO_2 to decompose 90% and the volume of dry N_2O gas produced at this point measured at STP are respectively
- (a) 6.978 hr, 2.016 L (b) 4.10 hr, 2.016 L
(c) 3.15 hr, 1.72 L (d) 2.35 hr, 1.56 L
28. Gold numbers of protective colloids A, B, C and D are 0.50, 0.01, 0.10 and 0.005 respectively. The correct order of their protective powers is
- (a) $D < A < C < B$ (b) $C < B < D < A$
(c) $A < C < B < D$ (d) $B < D < A < C$
29. Which of the following chemical reactions depicts the oxidising behaviour of H_2SO_4 ?
- (a) $2\text{HI} + \text{H}_2\text{SO}_4 \rightarrow \text{I}_2 + \text{SO}_2 + 2\text{H}_2\text{O}$
(b) $\text{Ca}(\text{OH})_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + 2\text{H}_2\text{O}$
(c) $\text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HCl}$
(d) $2\text{PCl}_5 + \text{H}_2\text{SO}_4 \rightarrow 2\text{POCl}_3 + 2\text{HCl} + \text{SO}_2\text{Cl}_2$
30. The half-life period of a radioactive element is 140 days. After 560 days, one gram of the element will reduce to
- (a) $(1/2)\text{ g}$ (b) $(1/4)\text{ g}$
(c) $(1/8)\text{ g}$ (d) $(1/16)\text{ g}$

SOLUTIONS

1. (d) : The structure of $\text{Na}_2\text{S}_4\text{O}_6$ is



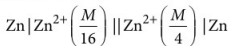
The two S atoms which are linked to each other have O.N. of zero. The O.N. of other two S-atoms can be calculated as follows :

$$2x + 2 \times 0 + 6 \times -2 = -2$$

$$\text{or } 2x = 12 - 2 = 10$$

$$\text{or } x = +5$$

2. (c) : The cell is,



$$\begin{aligned} \text{Now, } E_{\text{cell}} &= \frac{0.059}{2} \log \frac{C_2}{C_1} = \frac{0.059}{2} \log \frac{1}{4} \times \frac{16}{1} \\ &= \frac{0.059}{2} \times 2 \log 2 = 0.0178 \text{ V} \end{aligned}$$

3. (c) : If product concentration is x ,
for a zero order reaction, $\frac{x}{t} = k$

Thus, graph of x vs t would be a straight line passing through origin.

So, the given information is for zero order reaction.

For a zero order reaction, rate of the reaction is constant. Thus, plot of rate $\left(\frac{-d[X]}{dt} \right)$ vs time will be a straight line parallel to x -axis.

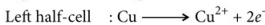
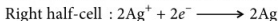
4. (b) : Colloidal solution of palladium has maximum surface area and so, can adsorb larger volume of hydrogen gas.

5. (a) : $\text{FeSO}_4 \xrightarrow{+2} \text{Fe}_2(\text{SO}_4)_3 \xrightarrow{+3}$

FeSO_4 present in Mohr's salt gets converted into $\text{Fe}_2(\text{SO}_4)_3$. This is a one-electron change and hence eq. wt. of Mohr's salt is equal to its mol. wt.

6. (d) : $\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$, $E^\circ_{\text{Cu}^{2+}|\text{Cu}} = 0.337 \text{ V}$
 $\text{Ag}^+ + e^- \longrightarrow \text{Ag}$, $E^\circ_{\text{Ag}^+|\text{Ag}} = 0.799 \text{ V}$

The cell reaction may be obtained as follows :



$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.799 - 0.337 \\ &= 0.462 \text{ V} \end{aligned}$$

Nernst equation is

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{2F} \ln \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2}$$

$$\text{For } E_{\text{cell}} = 0, 0 = 0.462 - \frac{0.0591}{2} \log \frac{0.01}{[\text{Ag}^+]^2}$$

$$\log \frac{0.01}{[\text{Ag}^+]^2} = \frac{2 \times 0.462}{0.0591} = 15.6345$$

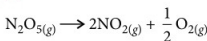
$$\log 0.01 - 2 \log [\text{Ag}^+] = 15.6345$$

$$2 \log [\text{Ag}^+] = \log 0.01 - 15.6345$$

$$\log [\text{Ag}^+] = \frac{-2 - 15.6345}{2} = -8.8173$$

$$[\text{Ag}^+] = 1.523 \times 10^{-9} \text{ M}$$

7. (b) : For the reaction :



$$\text{Rate} = -\frac{d[\text{N}_2\text{O}_5]}{dt} = k[\text{N}_2\text{O}_5]$$

For the reaction,



$$\text{Rate} = -\frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} = k'[\text{N}_2\text{O}_5]$$

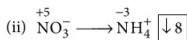
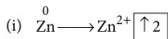
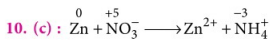
Since $-\frac{d[\text{N}_2\text{O}_5]}{dt}$ does not depend upon the way the chemical reaction is formulated, therefore

$$-\frac{d[\text{N}_2\text{O}_5]}{dt} = 2k'[\text{N}_2\text{O}_5] = k[\text{N}_2\text{O}_5] \Rightarrow k = 2k'$$

8. (c)

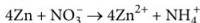
9. (b) : Let oxidation no. of I in I_3^- be x .

$$\therefore 3x = -1 \quad \therefore x = -\frac{1}{3}$$

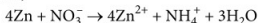


To make increase in O.N. = decrease in O.N. multiply eqn. (i) by 4 and add both the equations.

Hence,

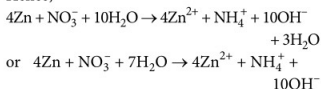


To balance O-atoms, add $3\text{H}_2\text{O}$ on RHS. Hence,



To balance H-atoms, add H_2O on LHS and 10OH^- on RHS.

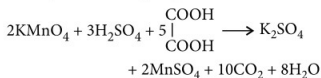
Hence,



11. (a)

12. (c) : Butter is colloidal system of water dispersed in fat.

13. (d) : Oxalic acid present in a solution can be determined by its titration with KMnO_4 solution in the presence of H_2SO_4 .



Titration cannot be done in the presence of HCl because KMnO_4 being a strong oxidizing agent oxidises HCl to Cl_2 and gets itself reduced to Mn^{2+} . So, actual amount of oxalic acid in solution cannot be determined.

14. (b) : Weight of Ag required

$$= 80 \times 5 \times 10^{-3} \times 1.05 \quad (\because \text{wt.} = \nu \times d)$$

$$= 0.42 \text{ g}$$

$$\therefore W = \frac{EIt}{96500}, \therefore 0.42 = \frac{108 \times 3 \times t}{96500}$$

$$\therefore t = 125 \text{ sec.}$$

15. (d) : For a zero order reaction, $t_{1/2}$ is given as

$$t_{1/2} = \frac{[A]_0}{2k} \quad \text{or} \quad k = \frac{[A]_0}{2t_{1/2}}$$

$$\text{Given, } t_{1/2} = 1 \text{ hr, } [A]_0 = 2 \text{ M}$$

$$\therefore k = \frac{2}{2 \times 1} = 1 \text{ mol L}^{-1} \text{ hr}^{-1}$$

Integrated rate law for zero order reaction is

$$[A] = -kt + [A]_0$$

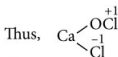
$$\text{Here, } [A]_0 = 0.5 \text{ M and } [A] = 0.25 \text{ M}$$

$$\Rightarrow 0.25 = -t + 0.5 \Rightarrow t = 0.25 \text{ hours.}$$

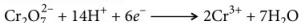
16. (a) : Since sol particles migrate towards cathode, they are positively charged. Hence, anions would be effective in coagulation. Greater is the valency of effective ion, greater is its coagulating power and smaller will be its coagulating value.

17. (d) : O.N. of Cl in $\text{Cl}^- = -1$

$$\text{O.N. of Cl in } \text{ClO}^- = +1$$



18. (c) : The reaction of $\text{Cr}_2\text{O}_7^{2-}$ in acidic medium can be shown as :



$$\therefore E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.059}{6} \log \frac{[\text{Cr}^{3+}]^2}{[\text{Cr}_2\text{O}_7^{2-}][\text{H}^+]^{14}}$$

$$= E_{\text{cell}}^\circ + \frac{0.059}{6} \log \frac{[\text{Cr}_2\text{O}_7^{2-}][\text{H}^+]^{14}}{[\text{Cr}^{3+}]^2}$$

$$= 1.33 + \frac{0.059}{6} \log \left(\frac{4.5}{1000} \right) \times (10^{-2})^{14}$$

$$\left(\frac{15}{1000} \right)^2$$

$$= 1.33 + \frac{0.059}{6} \log (2 \times 10^{-27})$$

$$= 1.33 + \frac{0.059}{6} \times [\log 2 - 27 \log 10]$$

$$= 1.33 - \frac{0.059 \times 26.69}{6} = 1.33 - 0.26 = 1.07 \text{ V}$$

19. (a) : For backward reaction, activation energy is the energy difference between the product and the activated complex.

CONCEPT MAP

GENERAL ORGANIC CHEMISTRY (Part-I)

- Introduction :
- Vital-force theory ("organic substances could originate only from living material") - by Berzelius.
 - Urea (NH_2CONH_2) was the 1st organic compound synthesised in lab by heating NH_4CNO - by F. Wöhler

Organic Compounds

Classification

Acyclic → Open-chain/Aliphatic

Cyclic → Closed-chain/Ring

Homocyclic (Carbocyclic)

Alicyclic

Aromatic

Benzenoid

Non-benzenoid

Heterocyclic

Non-aromatic (Alicyclic)

Aromatic

Isomerism

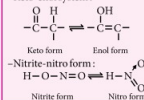
Structural

(Same molecular formula but different structural formulae)

- Chain (Nuclear/Skeleton) :** (Difference in the nature of the carbon chain).
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ (n-Butane) and $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_3$ (Isobutane)
- Position :** (Difference in the position of the substituent atom/group or an unsaturated linkage in the same C-chain).
 $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_3$ (But-1-ene) and $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$ (But-2-ene)
- Ring-chain :** (Difference in mode of linkage of C-atoms).
 $\text{CH}_3-\text{CH}=\text{CH}_2$ (Prop-1-ene) and Cyclopropane
- Functional :** (Difference in the nature of functional group).
 $\text{CH}_3\text{CH}_2\text{OH}$ and $\text{CH}_3-\text{O}-\text{CH}_3$ (Ethanol and Dimethyl ether)
- Metamerism :** (Difference in the nature of alkyl groups attached on either side of the same functional group).
 $\text{CH}_3-\text{O}-\text{C}_2\text{H}_5$ and $\text{C}_2\text{H}_5-\text{O}-\text{C}_2\text{H}_5$ (Methyl n-propyl ether and Diethyl ether)
- Tautomerism (Desmotropism) :** (Isomers exist in dynamic equilibrium);

Dyad system : If the H-atom oscillates between two polyvalent atoms linked together;
 $\text{H}-\text{C}\equiv\text{N} \rightleftharpoons \text{C}\equiv\text{N}-\text{H}$

Triad system : If the H-atom migrates from first polyvalent atom to third polyvalent atom within the same molecule in a chain.
 - Keto-enol system:



Breaking of a covalent bond

depends upon the electronegativity

Homolytic fission (Similar electronegativity)



$\dot{\text{C}}^+ + \text{X}^-$
 [Carbocation]
 (Electronegativity, $\text{C} < \text{X}$)

Heterolytic fission (Different electronegativity)



Stereoisomerism

Conformational

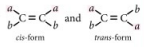
[Differ in the conformation]

Stability: staggered (anti) > skew or gauche > partially eclipsed > fully eclipsed

Configurational

Geometrical (cis-trans)

[Molecules have identical atomic organizations but different geometries]



Optical

[Rotate the plane polarised light]
 [Contain an asymmetric (chiral) carbon atom]



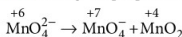
Have A Look!

- A few compounds of carbon such as CaCO_3 and LiCN are considered to be inorganic compounds.
- Pairs of compounds always form functional isomers with each other :
 - Dienes (allenes) and alkynes
 - Aldehydes, ketones and unsaturated alcohols
 - 1°, 2° and 3° amines
 - Cyanides and isocyanides
 - Alcohols and ethers
 - Carboxylic acids and esters
 - Nitroalkanes and alkyl nitrites
 - Aromatic alcohols, phenols and ethers
- Tautomerism term was introduced by 'Laar'.
- Benzophenone oxime, $(\text{C}_6\text{H}_5)_2\text{C}=\text{NOH}$ having two similar aryl groups does not show geometrical isomerism.
- Quartz was the first substance to exhibit the phenomenon of optical activity.
- Malic acid (saturated hydroxy dicarboxylic acid) $\xrightarrow{\text{show}}$ optical isomerism.
- Maleic acid (unsaturated dicarboxylic acid) $\xrightarrow{\text{show}}$ geometrical isomerism
- Conformational isomerism only found in alkanes, cycloalkanes and their derivatives.
- Anomers - Differ in configuration around C_1 -atom.
- Enantiomers - Mirror images but not superimposable.
- Diastereomers - Not mirror images with each other.

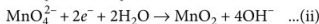
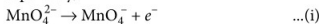
Free radical	Carbocation	Carbanion	Carbene
<ul style="list-style-type: none"> Electrically neutral, highly unstable, e^- deficient sp^2, planar Paramagnetic $\text{Ph}_3\dot{\text{C}} > \text{Ph}_2\dot{\text{C}}\text{H} > \text{Ph}\dot{\text{C}}\text{H}_2 > \text{CH}_2=\text{CH}-\dot{\text{C}}\text{H}_2 > 3^\circ > 2^\circ > 1^\circ$ e.g. - Wurtz reaction - Anti-Markownikoff's addition - Kolbe's electrolysis 	<ul style="list-style-type: none"> +ve charge on C, Electrophilic, Lewis acid sp^2, planar Diamagnetic $\text{Ph}_3\text{C}^+ > \text{Ph}_2\text{CH}^+ > \text{PhCH}_2^+ > \text{CH}_2=\text{CH}-\text{CH}_2^+ > 3^\circ > 2^\circ > 1^\circ$ e.g. - Pinacol-pinacolone rearrangement - Electrophilic addition reactions of alkenes, alkynes and aldehydes. - $\text{S}_{\text{N}}1$ reaction of R-X and diazonium salts 	<ul style="list-style-type: none"> -ve charge on C, Nucleophilic, Lewis base sp^3 (Non-conjugated), pyramidal sp^2 (Conjugated), planar Diamagnetic $\text{Ph}_3\text{C}^- > \text{Ph}_2\text{CH}^- > \text{PhCH}_2^- > \text{Allyl}^- > \text{CH}_3^- > 1^\circ > 2^\circ > 3^\circ$ e.g. - Aldol condensation - Cannizzaro's reaction - Perkin's reaction - Knoevenagel reaction 	<ul style="list-style-type: none"> Neutral, divalent with 2-unshared electrons Both nucleophilic and electrophilic (i) sp^2 (singlet): $\rightarrow \text{C}^-$ (Planar) ; (ii) sp (triplet): $\rightarrow \text{C}^-$ (Linear) (i) Diamagnetic (ii) Paramagnetic Stability: Triplet > Singlet e.g. - Carbylamine reaction - Reimer-Tiemann reaction - Wittig reaction - Wolff rearrangement

20. (d)

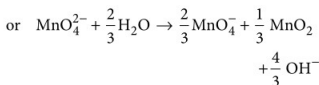
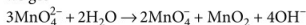
21. (a) : MnO_4^{2-} disproportionates as



We can consider the two half reactions separately,



Multiplying (i) by 2 and adding (i) and (ii), we get



Thus, 1 mole of MnO_4^{2-} disproportionates to $\frac{2}{3}$ mole of MnO_4^- and $\frac{1}{3}$ mole of MnO_2 .

22. (a) : Greater the reduction potential, stronger is the oxidizing agent. Hence, Y is stronger oxidizing agent than X but weaker than Z.

$$23. (a) : \ln \frac{k_2}{k_1} = \frac{\Delta H}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

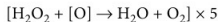
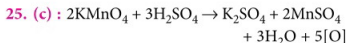
$$\ln \frac{6}{2} = \frac{\Delta H}{R} [1.5 \times 10^{-3} - 2 \times 10^{-3}]$$

$$1.09861 = \frac{\Delta H}{R} [-0.5 \times 10^{-3}]$$

$$\Rightarrow \Delta H = -\frac{1.09861 R}{0.5 \times 10^{-3}}$$

Since ΔH is -ve so, the reaction is exothermic.

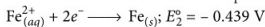
24. (d)



Thus, 1 mole KMnO_4 requires $\frac{5}{2}$ moles of H_2O_2 for decolourisation.

26. (c) : Given, $\text{Fe}_{(aq)}^{3+} + 3e^- \longrightarrow \text{Fe}_{(s)}$;

$$E_1^\circ = -0.036 \text{ V}$$



Required equation is



Applying $\Delta G^\circ = -nFE^\circ$

$$\text{and } \Delta G_3^\circ = \Delta G_1^\circ - \Delta G_2^\circ$$

$$(-n_3FE_3^\circ) = (-n_1FE_1^\circ) - (-n_2FE_2^\circ)$$

$$E_3^\circ = 3E_1^\circ - 2E_2^\circ$$

$$= 3 \times (-0.036) - 2 \times (-0.439)$$

$$E_3^\circ = -0.108 + 0.878 = 0.77 \text{ V}$$

$$27. (a) : k = \frac{2.303}{t} \log \frac{a}{(a-x)}$$

$$\frac{0.693}{2.1} = \frac{2.303}{t} \log \frac{100}{10} \quad \left[\because k = \frac{0.693}{t_{1/2}} \right]$$

$$\text{or } t = \frac{2.303}{0.33} \log 10$$

$$\text{or } t = 6.978 \text{ hr}$$

$$\text{Mole of } \text{NH}_2\text{NO}_2 \text{ taken} = \frac{6.2}{62} = 0.1$$

Number of moles of N_2O gas produced

$$= 0.1 \times \frac{90}{100}$$

Volume of N_2O gas produced at STP

$$= 0.09 \times 22.4 = 2.016 \text{ L}$$

28. (c) : For a protective colloid, lesser the value of gold number better is the protective power.

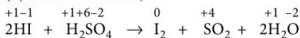
Thus, the correct order of protective power of

A, B, C and D is

Protective power : (A) < (C) < (B) < (D)

Gold number : $0.50 > 0.10 > 0.01 > 0.005$

29. (a) : In the reaction,



H_2SO_4 oxidises HI to I_2 and itself gets reduced to SO_2 and thus, acts as oxidising agent.

30. (d) : Since $T = n \times t_{1/2}$

$$560 = n \times 140; n = 4$$

$$\text{Now, } \frac{[A]}{[A]_0} = \left(\frac{1}{2}\right)^n = \left(\frac{1}{2}\right)^4 = \frac{1}{16}$$

Given, $[A]_0 = 1$

$$\frac{[A]}{1} = \frac{1}{16} \quad \therefore [A] = \frac{1}{16} \text{ g}$$



ADVANCED CHEMISTRY BLOC

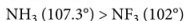
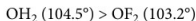
(CHEMICAL BONDING)

Mukul C. Ray, Odisha

VSEPR Theory

Relative bond angles involve many factors :

- In molecules of the type AB_2 or AB_3 , the $B-A-B$ bond angles decrease with increasing electronegativity of atom B . For example, bond angles follow the order :



- But the bond angle in PF_3 (97.7°) is greater than that of PH_3 (93.2°). This is also for the case AsH_3 (91.8°) and AsF_3 (96.2°).

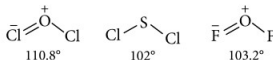
For a fluorine containing compound of third period element, for example PF_3 , multiple bonding ($p\pi-d\pi$) is possible.



The greater bond order ($\sigma + \pi$ bonding) increases the electron density and increases the repulsion among the bonding electrons. But the bond angles for phosphorus halides increase in the order : $PF_3 < PCl_3 < PBr_3 < PI_3$. The effect of decrease in bond order probably has been offset by the increasing size of the bonding orbital.

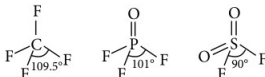
Does it look irrational when fluorine carries the positive charge? No, fluorine is a strong electronegative element with respect to sigma bond but it is a pi-electropositive element owing its small size.

- VSEPR theory suggests that multiple bonds exert a stronger repulsion than single bonds and the molecule adjusts its geometry to reflect this.

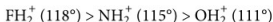
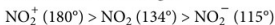


Sulphur being larger in size does not feel like delocalising the lone pair towards chlorine.

How the double bonds influence the bond angles are also clear from the following examples :



- Number of electrons on the central atom also influences the bond angle.

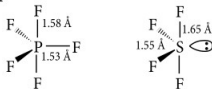


TBP (Trigonal Bipyramidal) an irregular geometry

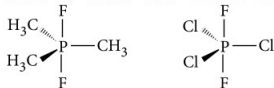
Unlike octahedral structure where the distance up to any atom starting from the center is identical; TBP has a different geometry. The axial bonds are here longer than equatorial bonds. These are best explained by saying the sp^3d as sp^2pd hybridisation.

The Structural Generalisations :

- The axial bonds are generally longer than equatorial bonds in a TBP geometry. The difference becomes larger as the number of lone pairs is increased.



- More electronegative substituents favour the axial site than equatorial site. This is the **Bent's rule**. The electronegative atom comes up in the axial position because in that direction, the *p*-character is more in the sp^3d hybrids. This would help the electronegative atoms to fulfill their electron demands.

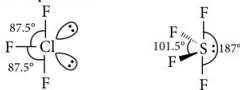


Electronegativity of $-F$ is higher than $-Cl$ and $-CH_3$.

- Multiple bonds generally occupy the equatorial position. Since they exert more repulsion and the molecule distorts.



- The lone pair of electrons occupies the equatorial position.



Dipole Moment

Vector addition may not give right result in dipole moment :

- If the dipole moment of chlorobenzene is 1.54 D, as per vector addition rule ($\mu_{res} \approx \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos \theta}$) dipole moment of 1,2-dichlorobenzene should be 2.5 D but instead it is observed as 2.14 D.



(Less) 1.54 D



(More) 2.14 D

- Similarly, the dipole moment of chlorobenzene and 1,3-dichlorobenzene should be equal as per the rules of vector addition. But, practically the later has a dipole moment value different than 1.68 D.
- Another similar example of a pair of compounds is CH_3Cl and $CHCl_3$. As per rules, these two compounds would have identical values of dipole moments but sensibly while the former has a dipole moment value of 1.87 D, the later has a value of only 1.01 D.

Some dipole moment values :

Molecule	Dipole moment (D)	Molecule	Dipole moment (D)
H ₂ O	1.85	NH ₃	1.47
HF	1.91	CH ₃ OH	1.71
C ₂ H ₅ OH	1.69	HCl	1.08
CH ₃ Cl	1.87	CH ₂ Cl ₂	1.57

High value of dipole moment results high boiling point :

Molecule	Dipole moment (D)	Boiling point (K)
Propane	0.1	231
Dimethyl ether	1.3	248
Chloromethane	2.0	249
Acetaldehyde	2.7	294
Acetonitrile	3.9	355

Bond length has its role in dipole moment : The dipole moment of methyl fluoride is expected to be higher than methyl chloride because of larger polarity but practically the dipole moment value of methyl chloride is 1.87 D whereas that of methyl fluoride is 1.851 D. This is surely due to higher bond length of methyl chloride.

Hybridisation

Hydrogen sulphide has no hybridisation :

- Hybridisation is a wonderful concept and is taught in every general class of chemistry but it has serious limitations particularly for elements below the full second row of the periodic table.
- The bonded state of H_2O molecule is explained by saying that it is sp^3 hybridised. Such hybrid orbitals are more energetic than s -orbital and less energetic than p -orbitals. By placing the non-bonding electron of $2s$ -orbital in the hybridised orbital it has made the system unstable.
- But there are few advantages too. Now the two lone pairs $2s^2$ and $2p_x^2$ of oxygen atom are largely separated in space thus lowering the repulsion energy and the second advantage is that the system is making more stronger overlaps by using hybrid orbitals than what it would have gained by using pure orbitals.
- Now, the sp^3 hybridisation for H_2S , H_2Se etc. can be predicted. Instead, the bond angles in these three molecules are nearly 90° , as if the p -orbitals were not hybridised at all! One important reason for the difference is the extra radial nodes in hybridised orbital with $n > 2$. The $3p_z$ -orbital has four lobes and the $3s$ -orbital has two radial nodes, so it is difficult to produce a large node free region for a favourable sigma bond. The energy gained by creating a slightly improved bonding region does not overcome the energy difference between $3s$ and $3p$ -orbitals.
- The index of hybridization is not necessarily a whole number.

$$\cos \theta = \frac{s}{s-1}$$

where 's' is the degree of s -character.

The bond angle between the hybrid orbitals when is 107.1° , the hybridisation is $sp^{3.4}$. The gradual decrease in bond angles from 180° , lowers the s -character in the hybrid orbitals.

Molecular Orbital Theory

Bond order of CO^+ cannot be more than three :

- The energy difference between the $2s$ and $2p$ -orbitals of B is only 5.7 eV whereas that for F is 21.6 eV . The MO energy order will be followed in case of oxygen when there is large energy difference between the interacting orbitals. When the interacting orbitals are close in energy, the resulting MOs of same symmetry type and same energy type interact with each other. This may be looked upon as mixing of orbitals—similar to hybridisation in VBT.
- During this mixing the, pi-bonding and antibonding orbitals do not find orbitals of proper symmetry and energy to interact and thus remain free from mixing of orbitals event. For this reason, MOs are represented as σ_1, σ_2^* etc. not $\sigma_{2s}, \sigma_{2s}^*$ etc. Due to mixing, the lower energy MO is further lowered in energy and higher energy MO is further raised in energy. Thus, there is a different energy order for N_2, B_2 etc.
- The idea with which the homonuclear diatomic molecules is dealt with can well be applied on heteronuclear diatomic molecules. The main difference is that the participating atomic orbitals do not usually have the same energy.
- When the bonding is in between same element, the overlapping is most efficient and the covalent bond energy is at its maximum (figure-a).

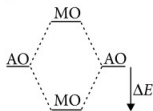


Fig. (a) : MO diagram involving atoms of equal electronegativity.

- When one atom is more electronegative than the second, the energy mismatch causes poor overlapping of orbitals and covalent bond energy is less (figure-b).

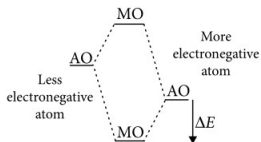


Fig. (b) : MO diagram involving atoms of different electronegativities.

- Less covalent bond energy does not necessarily mean that the bond is weak. The exact nature of bonding varies (polarisation of ionic bond and polarity of covalent bond) between purely covalent at one end to purely ionic at the other end. Therefore, the total bonding energy in one situation is the sum of covalent and ionic contributions. The situation shown in (figure-b) has poor covalent contribution,

at least as compared to the (figure-a) but may have a strong ionic contribution.

- In the MO diagram of CO, the atomic orbitals of carbon atom are more energetic than the atomic orbitals of oxygen atom. The form of the diagram is slightly asymmetric. The ordering of the MO energy levels is very same as that observed in nitrogen.
- Similar applications to other species give the following results :
 - The pair of electrons in σ_1 corresponds the carbon-oxygen σ bond.
 - The pairs of electrons in σ_2^* and σ_3 orbitals correspond to lone pairs; the former is largely on oxygen and the later on carbon.
- Some examples of molecules and ions are given below :

Species	MO Configuration	Bond order	No. of unpaired electrons
CO	$(\sigma_1)^2 < (\sigma_2^*)^2 < (\pi)^2 = (\pi)^2 < (\sigma_3)^2$	3	0
NO	$(\sigma_1)^2 < (\sigma_2^*)^2 < (\pi)^2 = (\pi)^2 < (\sigma_3)^2 < (\pi^*)^1 = (\pi^*)^0$	2.5	1
NO ⁺	$(\sigma_1)^2 < (\sigma_2^*)^2 < (\pi)^2 = (\pi)^2 < (\sigma_3)^2$	3	0
CN ⁻	$(\sigma_1)^2 < (\sigma_2^*)^2 < (\pi)^2 = (\pi)^2 < (\sigma_3)^2$	3	0

- On moving from CO to CO⁺, the carbon-oxygen bond length decreases from 112.8 pm to 111.5 pm. Many books write the bond order increases to 3.5 with the removal of one electron from σ_2^* orbital. But with involvement of *p*-orbitals the bond order can never be more than three. Note that with involvement of *d*-orbital, bond

order of even four is possible. An alternative reasonable explanation is with a triple bond. There is partial dative bond character. Due to ionisation, the species has developed a net charge, which is now distributed between the atoms. This modification of character of bond is responsible for decrease in bond length.

**Essential Facts in
Physics, Chemistry & Biology**

- Learn how to study effectively
- How to manage time
- How to improve concentration
- How to solve MCQ's

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Jammu & Kashmir Common Entrance Test

- What is the unit of zero order reaction?
(a) mol L s^{-1} (b) s^{-1}
(c) $\text{L mol}^{-1} \text{s}^{-1}$ (d) None of these.
- The chief commercial use of amines as intermediates in the synthesis of
(a) medicines
(b) fibres
(c) medicines and fibres
(d) proteins.
- The colour of transition metal compound is due to
(a) complete ns -subshell
(b) small size metal ions
(c) incomplete $(n-1)d$ -subshell
(d) absorption of light in UV region.
- The concentration of hydrogen ion in a sample of soft drink is $3.8 \times 10^{-3} \text{ M}$. What is its pH?
(a) 3.84 (b) 2.42
(c) 4.44 (d) 1.42
- Based on which method amines are prepared?
(a) Reduction of nitro compounds
(b) Ammonolysis of alkyl halides
(c) Reduction of nitriles and amides
(d) All of the above.
- EDTA can form complex with how many number of donor atoms?
(a) One (b) Two
(c) Six (d) Three
- According to IUPAC system, what is the correct name of the compound $[\text{Cr}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{Cl}_3$?
(a) Triamminetriaquachromium(III) chloride
(b) Triamminetriaquachromium chloride(III)
(c) Tetraammoniumtriaquachromium(III) chloride
(d) None of the above.
- What is the value of $1/n$, in Freundlich adsorption isotherm?
(a) Between 2 and 4 in all cases
(b) Between 0 and 1 in all cases
(c) 1 in case of chemisorptions
(d) 1 in case of physical adsorption
- The smallest quantity of energy that can be emitted or absorbed in the form of electromagnetic radiation is known as
(a) quantum (b) photon
(c) spectrum (d) photoelectron.
- Monovalent sodium and potassium ions, divalent magnesium and calcium ions are found in
(a) lipids (b) biological fluids
(c) fats (d) enzymes.
- Anti-Markovnikov addition of HBr is observed in
(a) propene (b) but-2-ene
(c) pent-2-ene (d) all of these.
- What is conductance?
(a) Inverse of resistance
(b) Proportional of resistance
(c) Equal of resistivity
(d) Equal of resistance
- The total number of orbitals associated with the principal quantum number $n = 3$, is
(a) 9 (b) 8
(c) 5 (d) 7

14. It has been found that for a chemical reaction with rise in temperature by 10° , the rate constant is
(a) nearly doubled (b) nearly tripled
(c) increases 5 times (d) increases 4 times.
15. Which is the metal present in the coordination compound chlorophyll?
(a) Ca (b) Mg
(c) K (d) Na
16. Ethylene can be converted into alcohol by treatment of
(a) aq.KOH (b) H_2SO_4 as catalyst
(c) moist silver oxide (d) Zn/HCl .
17. Why *d*-block elements form complexes?
(a) Due to large size and high nuclear charge.
(b) Due to small size and low nuclear charge.
(c) Due to small size and high nuclear charge.
(d) None of these.
18. Which among the following is a non-colligative property?
(a) Elevation in boiling point
(b) Osmotic pressure
(c) Refractive index
(d) Lowering of vapour pressure
19. What kinds of bonds are present in ethene molecule?
(a) 1 pi and 5 sigma bonds
(b) 1 pi and 3 sigma bonds
(c) 1 sigma and 1 pi bond
(d) 3 sigma and 3 pi bonds
20. In which year, IUPAC draft recommends that anionic ligands will end with-ido so that chloro would become chlorido?
(a) 1994 (b) 1984
(c) 2000 (d) 2004
21. What is the IUPAC name of isopropylamine?
(a) Propan-2-amine (b) Ethanamine
(c) 2-Aminotoluene (d) Propan-1-amine
22. Which factor has no influence on the rate of reaction?
(a) Molecularity
(b) Temperature
(c) Concentration of reactant
(d) Nature of reactant
23. Negatively charged particles are called
(a) electrons (b) protons
(c) neutrons (d) none of the above.
24. Who has synthesised the organic compound 'urea' for the first time?
(a) Friedrich Wöhler (b) Berzelius
(c) Kolbe (d) Berthelot
25. Mass number of an atom is the sum of
(a) number of protons + number of neutrons + number of electrons
(b) number of protons + number of neutrons
(c) number of protons + number of electrons
(d) number of electrons + number of neutrons.
26. The mixture of reactants and products in the equilibrium state is called
(a) chemical mixture
(b) equilibrium mixture
(c) chemical equilibrium
(d) dynamic equilibrium.
27. The relative ease of dehydration of alcohols follows following order
(a) tertiary > secondary > primary
(b) primary > secondary > tertiary
(c) secondary > tertiary > primary
(d) tertiary > primary > secondary.
28. Which one of the following acids does NOT have a carboxylic group?
(a) Methanoic acid (b) Ethanoic acid
(c) Propanoic acid (d) Picric acid
29. What elements are present in *f*-block series?
(a) Lanthanoids
(b) Actinoids
(c) Lanthanoids and actinoids
(d) Lipids
30. What is the type of hybridisation found in methane?
(a) sp^3 (b) sp^2
(c) sp^1 (d) None of these.
31. Which is the correct statement about solid?
(a) Very high compressibility
(b) Maximum intermolecular distance
(c) Definite mass but no definite volume
(d) Maximum intermolecular force of attraction

32. Compounds having the same molecular formula but different structures are classified as
- functional group isomers
 - structural isomers
 - optical isomerism
 - metamerism.
33. What kind of isomerism is exhibited by the compounds $\text{CH}_3\text{CH}_2\text{CHO}$ and CH_3COCH_3 ?
- Geometrical isomerism
 - Functional isomers
 - Tautomers
 - Metamers
34. Food preservatives prevent spoilage of food due to microbial growth. The most commonly used preservatives are
- table salt, sugar
 - vegetable oils and sodium benzoate
 - $\text{C}_6\text{H}_5\text{COONa}$
 - all of the above.
35. Which compound is responsible for perfumery?
- Ketones
 - Ethers
 - Alcohols
 - Esters
36. The process of formation of polymers from respective monomers is called
- polyacrylonitrile
 - copolymerisation
 - polymerisation
 - none of the above.
37. The colour in the coordination compounds can be readily explained in terms of
- spectrochemical
 - chelate effect
 - crystal field theory
 - none of the above.
38. Paramagnetism is exhibited due to which one of the following reason?
- Presence of unpaired electrons
 - Presence of completely filled electronic subshell
 - By non-transition element
 - By elements with noble gas configuration
39. Which of the following mentioned is a type of hydrocarbon?
- Saturated hydrocarbons
 - Unsaturated hydrocarbons
 - Aromatic hydrocarbons
 - All of the above.
40. The removal of an electron from an atom results in the formation of
- anion
 - anode
 - cation
 - cathode.
41. 45 g of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) is mixed with 600 g of water, what is the depression of freezing point?
- 7.9 K
 - 2.5 K
 - 6.6 K
 - 2.2 K
42. Addition of oxygen to an element or a compound is termed as
- oxidation
 - reduction
 - ionisation
 - redox reaction.
43. Mass of a proton is
- 0.00727 amu
 - 1.0087 amu
 - 0.00054 amu
 - 1.00727 amu.
44. What is the product of reaction between calcium carbide and water?
- Ethylene
 - Acetylene
 - Methane
 - Benzene
45. Among the following molecules, which has the zero dipole moment?
- BF_3
 - H_2O
 - NF_3
 - ClO_2
46. What colour is imparted into the flame when lithium is burnt?
- Golden yellow
 - Brick red
 - Crimson red
 - Grassy green
47. Henry's law constant value for O_2 in water is
- 46.82
 - 43.86
 - 88.84
 - 76.48
48. Sodium carbonate is manufactured by
- Castner-Kellner
 - Solvay process
 - Oxidation
 - Transmission process.
49. Which acid is present in vinegar?
- Formic acid
 - Acetic acid
 - Butyric acid
 - Tartaric acid

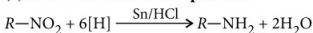
50. The attractive force which holds various constituents together in different chemical species is called
(a) valence bond (b) chemical bond
(c) atomic bond (d) electrovalent bond.
51. Silver, gold, platinum, iron, copper and titanium are part of the
(a) minerals (b) transition metals
(c) salts (d) all of the above.
52. Molality of 2.5 g of ethanoic acid (CH_3COOH) in 75 g of benzene is
(a) $0.565 \text{ mol kg}^{-1}$ (b) $0.656 \text{ mol kg}^{-1}$
(c) $0.556 \text{ mol kg}^{-1}$ (d) $0.665 \text{ mol kg}^{-1}$
53. Polycondensation products of dicarboxylic acids and diols are
(a) polyamides (b) neoprene
(c) glyptal (d) polyesters.
54. When acetaldehyde is heated with dilute sodium hydroxide solution, the product is
(a) ethanol and sodium acetate
(b) paraldehyde
(c) aldol
(d) brown resin.
55. Gas constant is equal to the
(a) product of two specific heats
(b) difference of two specific heats
(c) ratio of two specific heats
(d) sum of two specific heats.
56. How many octahedral void(s) are present per atom in a cubic close-packed structure?
(a) 3 (b) 4
(c) 1 (d) 2
57. The enthalpy change accompanying a reaction is called
(a) reaction enthalpy
(b) standard enthalpy
(c) thermochemical equation
(d) enthalpy of atomization.
58. In Br_3O_8 compound, oxidation number of bromine is
(a) 16/13 (b) 26/3
(c) 24/3 (d) 16/3
59. How much is the pH of human blood?
(a) 5.2 (b) 8.3
(c) 6.3 (d) 7.4
60. How will you define the specific heat at constant volume?
(a) The amount of heat required to raise the temperature of unit mass of gas through one degree, at constant pressure.
(b) The amount of heat required to raise the temperature of 1 kg of water through one degree.
(c) The amount of heat required to raise the temperature of unit mass of gas through one degree at constant volume.
(d) All of these.
61. All substances that conduct electricity in aqueous solutions are called
(a) electrolytes (b) acids
(c) buffers (d) catalyst.
62. Energy of one mole of photons of radiation whose frequency is $5 \times 10^{14} \text{ Hz}$ is
(a) $199.51 \text{ kJ mol}^{-1}$ (b) $189.51 \text{ kJ mol}^{-1}$
(c) $198.51 \text{ kJ mol}^{-1}$ (d) $188.51 \text{ kJ mol}^{-1}$
63. Carbonyl compounds are constituents of
(a) fabrics, drugs
(b) fabrics, plastics
(c) flavourings, plastics
(d) all of the above.
64. In the formation of π -bond, the atomic orbitals overlap in such a way that
(a) their axes remain parallel to each other and perpendicular to the internuclear axis
(b) their axes remain parallel to each other and parallel to the internuclear axis
(c) their axes remain perpendicular to each other and parallel to the internuclear axis
(d) their axes remain perpendicular to each other and perpendicular to the internuclear axis.
65. Lithium shows diagonal relationship with
(a) sodium (b) magnesium
(c) calcium (d) aluminium.

66. Use of chemicals for therapeutic effect is called
 (a) medicines
 (b) chemotherapy
 (c) drug-target interaction
 (d) phototherapy.
67. Atoms with identical atomic number but different atomic mass number are known as
 (a) polymers (b) isobars
 (c) isotopes (d) isomers.
68. Ionization energy and electron affinity are defined at
 (a) enthalpy (b) spontaneity
 (c) equilibrium (d) absolute zero.
69. Wood spirit is known as
 (a) ethanol (b) methanol
 (c) propanol (d) none of these.
70. The crystal lattice of electrovalent compound is composed of
 (a) oppositely charged ions
 (b) both molecules and ions
 (c) molecules
 (d) atoms.
71. What is the percentage of free space in body-centred cubic unit cell?
 (a) 32% (b) 20%
 (c) 34% (d) 28%
72. What are the lanthanides and actinides?
 (a) Inner-transition elements
 (b) Noble gases
 (c) Normal elements
 (d) Transition elements
73. A reagent which lowers the oxidation number of an element in a given substance is known as
 (a) oxidising agent (b) reduction
 (c) reducing agent (d) oxidation.
74. Which of the following is used in the manufacture of alloys?
 (a) Lithium (b) Halides
 (c) Plaster of Paris (d) Beryllium
75. Williamson's synthesis is used to prepare
 (a) acetone (b) PVC
 (c) ethers (d) bakelite.

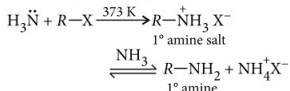
SOLUTIONS

1. (d): The unit of rate constant, k for zero order reaction is $\text{mol L}^{-1} \text{s}^{-1}$.
2. (c): The chief commercial use of amines as intermediates in the synthesis of dyes, synthetic fibres, medicines, etc. due to physiological and psychological effects.
3. (c)
4. (b): $\text{pH} = -\log [\text{H}^+] = -\log(3.8 \times 10^{-3})$
 $= -[\log(3.8) + \log(10^{-3})]$
 $= -[(0.58) + (-3.0)]$
 $= -(-2.42) = 2.42$
- Therefore, the pH of the soft drink is 2.42 and it can be inferred that it is acidic.
5. (d): Amines are prepared by all the given methods:

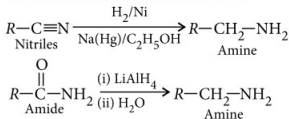
(a) Reduction of nitro compounds:



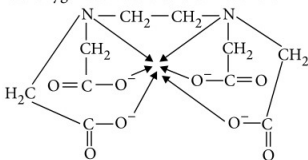
(b) Ammonolysis of alkyl halides:



(c) Reduction of nitriles and amides:



6. (c): EDTA ion (EDTA^{4-}) is a hexadentate ligand. It can bind through two nitrogen and four oxygen atoms to a central metal ion.



Ethylenediaminetetraacetate ion (EDTA^{4-})

7. (a): The IUPAC name of the complex, $[\text{Cr}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{Cl}_3$ is triamminetriaquachromium(III) chloride.

8. (b): For Freundlich adsorption isotherm,

$$\log \frac{x}{m} = \log k + \underbrace{\frac{1}{n}}_{\text{intercept}} \log P$$

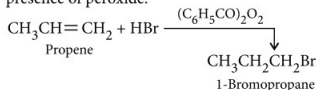
$$\underbrace{\frac{1}{n}}_{\text{slope}}$$

The factor $\frac{1}{n}$ can have values between 0 and 1 in all cases.

9. (a): Planck gave the name 'quantum'.

10. (b): Monovalent sodium and potassium ions and divalent magnesium and calcium ions are found in large proportions in biological fluids. These ions perform important biological functions such as maintenance of ion balance and nerve impulse conduction.

11. (a): Anti-Markovnikov addition is observed in unsymmetrical alkenes like propene in presence of peroxide.



12. (a): The inverse of resistance, R is called conductance, G . The relation is,

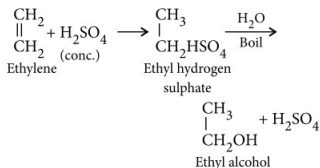
$$G = \frac{1}{R}$$

13. (a): By using the relation,
no. of orbitals = $n^2 = (3)^2 = 9$

14. (a)

15. (b): The pigment chlorophyll is responsible for photosynthesis. It is a coordination compound of magnesium.

16. (b): In the presence of a few drops of conc. H_2SO_4 , ethylene reacts with water to form ethyl alcohol, in accordance with Markovnikov rule.

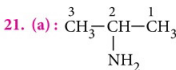


17. (c): The d -block elements form a large number of complex compounds due to comparatively smaller sizes of the metal ions, their high ionic charges and the availability of d -orbitals for bond formation.

18. (c)



20. (d)



Common name : Isopropylamine

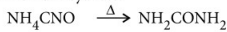
IUPAC name : Propan-2-amine

22. (a): The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction is called molecularity and it has no influence on the rate of reaction.

23. (a):

Particles	Symbol	Relative charge
Electrons	e	-1
Protons	p	+1
Neutrons	n	0

24. (a): Friedrich Wöhler synthesised an organic compound, urea from an inorganic compound, ammonium cyanate.



Ammonium cyanate

Urea

25. (b): The total number of nucleons is termed as mass number (A) of the atom.

Hence, Mass number (A)

= No. of protons (Z) + No. of neutrons (n)

26. (b)

27. (a)

28. (d): Methanoic acid - HCOOH

Ethanoic acid - CH_3COOH

Propanoic acid - $\text{CH}_3\text{CH}_2\text{COOH}$

Picric acid - 

2, 4, 6-Trinitrophenol
(Picric acid)

29. (c) : The *f*-block consists of the two series—lanthanoids and actinoids.

30. (a) :

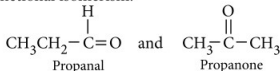


Methane (CH_4) exhibits sp^3 hybridisation.

31. (d) : (a) Solids are incompressible and rigid.
(b) Their internuclear distances are short.
(c) They have definite mass, volume and shape.

32. (b)

33. (b) : The molecular formula, $\text{C}_3\text{H}_6\text{O}$ represents an aldehyde and ketone and they exhibit functional isomerism.



34. (d)

35. (d)

36. (c)

37. (c) : The crystal field theory (CFT) is successful in explaining the formation, structure, colour and magnetic properties of coordination compounds to a large extent.

38. (a) : The substances having unpaired electrons show paramagnetism.

39. (d) : Depending upon the types of carbon-carbon bonds present, hydrocarbons can be classified into three main categories—

- Saturated hydrocarbons contain C—C single bonds.
- Unsaturated hydrocarbons contain C=C or $\text{C}\equiv\text{C}$ bonds.
- Aromatic hydrocarbons are special type of cyclic compounds.

40. (c) : $X_{(g)} \rightarrow X_{(g)}^+ + e^-$
Atom Cation

41. (d) : Using relation,

$$\Delta T_f = \frac{k_f \times w_2 \times 1000}{M_2 \times w_1}$$

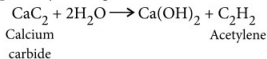
[k_f for water = $1.86 \text{ K kg mol}^{-1}$]

$$\Delta T_f = \frac{1.86 \times 45 \times 1000}{62 \times 600} = 2.25 \text{ K}$$

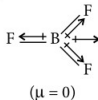
42. (a)

43. (d)

44. (b) : On industrial scale, ethyne (acetylene) is prepared by treating calcium carbide with water.



45. (a) : In BF_3 , the dipole moment is zero although the B—F bonds are oriented at an angle of 120° to one another, the three bond moments give a net sum of zero as the resultant of any two is equal and opposite to the third.



46. (c)

47. (a) : The value of Henry's law constant, k_H for $\text{O}_{2(g)}$ in water at 303 K is 46.82 kbar.

48. (b)

49. (b)

50. (b)

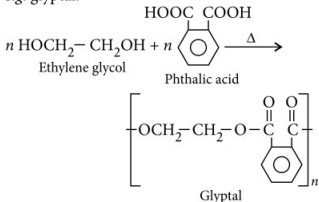
51. (b)

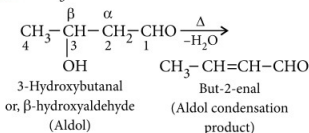
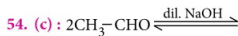
52. (c) : Molar mass of $\text{C}_2\text{H}_4\text{O}_2$, M_B
 $= 12 \times 2 + 1 \times 4 + 16 \times 2 = 60 \text{ g mol}^{-1}$

$$\text{Molality, } m = \frac{w_B \times 1000}{M_B \times w_A}$$

$$m = \frac{2.5 \times 1000}{60 \times 75} = 0.556 \text{ mol kg}^{-1}$$

53. (d) : In polycondensation reaction, the two bi-functional monomers *i.e.*, dicarboxylic acids and diols react and form the high molecular mass condensation polymers *i.e.*, polyesters. *e.g.* glyptal.





55. (b): A relation that connects the specific heats C_p , C_v and the gas constant, R is

$$\boxed{C_p - C_v = R}$$

56. (c) : Octahedral void per unit cell of *ccp* at the body-centre of the cube = 1

12 octahedral voids located at each edge and shared between four unit cells = $12 \times \frac{1}{4} = 3$

∴ Total number of octahedral voids = 4
In *ccp* structure, each unit cell has 4 atoms.
Thus, number of octahedral voids is equal to 4.
Hence, number of octahedral voids per atom

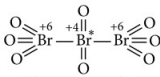
$$= \frac{4}{4} = 1$$

57. (a) : In a chemical reaction,



The enthalpy change accompanying a reaction is called the reaction enthalpy, given by the symbol $\Delta_r H$.

58. (d) : In Br_3O_8 compound, each of the two terminal bromine atoms are present in +6



Tribromooctaoxide, Br_3O_8

oxidation states and the middle bromine is present in +4 oxidation state. Hence, the oxidation number of bromine is 16/3.

59. (d) : The pH of human blood is slightly alkaline i.e., 7.4.

60. (c) 61. (a)

62. (a) : Energy (E) of one photon is given by the expression, $E = h\nu$

$$h = 6.626 \times 10^{-34} \text{ J s}$$

$$\nu = 5 \times 10^{14} \text{ s}^{-1} \text{ (given)}$$

$$E = (6.626 \times 10^{-34} \text{ J s}) \times (5 \times 10^{14} \text{ s}^{-1})$$

$$= 3.313 \times 10^{-19} \text{ J}$$

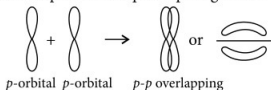
Energy of one mole of photons

$$= (3.313 \times 10^{-19} \text{ J}) \times (6.022 \times 10^{23} \text{ mol}^{-1})$$

$$= 199.51 \text{ kJ mol}^{-1}$$

63. (d)

64. (a) : During π -bond formation, the orbitals formed due to sidewise overlapping consists of two saucer type charged clouds above and below the plane of the participating atoms.



65. (b)

66. (b)

67. (c)

68. (d)

69. (b) : Methanol, CH_3OH , also known as 'wood spirit', was produced by destructive distillation of wood.

70. (a)

71. (a) : In *bcc* structure, total number of atoms is 2

$$\text{and their volume is } 2 \times \left(\frac{4}{3} \right) \pi r^3$$

$$\text{Volume of cube, } a^3 = \left(\frac{4}{\sqrt{3}} r \right)^3$$

Therefore, Packing efficiency

Volume occupied by two spheres in

$$= \frac{\text{the unit cell} \times 100}{\text{Total volume of the unit cell}}$$

$$= \frac{2 \times (4/3)\pi r^3 \times 100}{[(4/\sqrt{3})r]^3} = \frac{(8/3)\pi r^3 \times 100}{64r^3/3\sqrt{3}} = 68\%$$

Hence, the free space is $100 - 68 = 32\%$.

72. (a) : The two rows of elements at the bottom of the periodic table, called the lanthanides and actinides. The last electron added to each element is filled in *f*-orbital. Hence, they are called inner-transition elements (*f*-block elements).

73. (c) : Reducing agents, lower the oxidation number of an element. These reagents are also called as reductants.

74. (d) : Copper-beryllium alloys are used in the preparation of high strength springs.

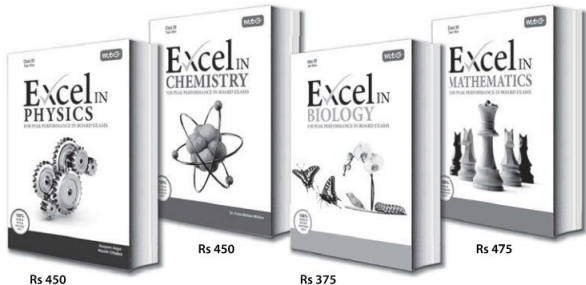
75. (c) : $\text{R-X} + \text{R'-O}^+ \text{Na} \longrightarrow \text{R-O-R'} + \text{NaX}$

Alkyl halide

Ether



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CHAPTERWISE PRACTICE PAPER

Series-4

The p-Block Elements (Group 15 to 18)

Time : 3 hrs.

Marks : 70

GENERAL INSTRUCTIONS

- (i) All questions are compulsory.
- (ii) Question numbers 1 to 8 are very short-answer questions and carry 1 mark each.
- (iii) Question numbers 9 to 18 are short-answer questions and carry 2 marks each.
- (iv) Question numbers 19 to 27 are also short-answer questions and carry 3 marks each.
- (v) Question numbers 28 to 30 are long-answer questions and carry 5 marks each.
- (vi) Use Log Tables, if necessary. Use of calculator is not allowed.

1. Why is N_2 less reactive at room temperature?
 2. Why is dioxygen a gas but sulphur a solid?
 3. Which is a strong acid in aqueous solution, HF or HCl?
 4. Balance the following equation :
 $XeF_6 + H_2O \rightarrow XeO_2F_2 + HF$
 5. What is the basicity of H_3PO_4 ?
 6. Write the order of thermal stability of the hydrides of group-16 elements.
 7. Why does fluorine form only one oxoacid, HOF?
 8. Noble gases have very low boiling points. Why?
 9. State the difference in properties of white and red phosphorus.
 10. Give two examples to show the anomalous behaviour of fluorine.
- OR**
- Complete the reactions :
- (i) $Ca(OH)_2(dil.) + Cl_2 \rightarrow$
 - (ii) $F_2 + H_2O (hot) \rightarrow$
11. Arrange the following in the order of property indicated for each set :
 - (i) F_2, Cl_2, Br_2, I_2 - Increasing bond dissociation enthalpy.
 - (ii) HF, HCl, HBr, HI - Increasing acid strength.
 12. Complete the following reactions :
 - (i) $XeF_4 + O_2F_2 \rightarrow$
 - (ii) $XeF_4 + SbF_5 \rightarrow$
 13. Can PCl_5 act as an oxidizing as well as a reducing agent? Justify.
 14. Write the structure of the following species :
 - (i) H_2SO_5
 - (ii) H_2SO_3
 15. Complete the following chemical equations :
 - (i) $NaOH(aq) + Cl_{2(g)} (hot\ and\ conc.) \rightarrow$
 - (ii) $I_2 + HNO_3 \rightarrow$
 16. (i) Draw the structure of XeF_6 .
(ii) Does the hydrolysis of XeF_6 lead to a redox reaction?
 17. Assign a reason for each of the following :
 - (i) In group 15, the bond angle H-M-H decreases in the following order :
 $NH_3(107.8^\circ) > PH_3(93.6^\circ) > AsH_3(91.8^\circ)$
 - (ii) Increasing base strength order is :
 $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$.

18. What happens when sulphur dioxide is passed through an aqueous solution of Fe(III) salt?
19. Give reasons :
- Noble gases are mostly inert.
 - Neon is generally used for warning signals.
 - Noble gases have largest radii.
20. Give the formula and describe the structure of a noble gas species which is isostructural with :
- ICl_4^-
 - IBr_2^-
 - BrO_3^-
21. (i) Why does $\text{R}_3\text{P}=\text{O}$ exist but $\text{R}_3\text{N}=\text{O}$ does not (R = alkyl group)?
 (ii) Why is BiH_3 the strongest reducing agent amongst all the hydrides of group-15 elements?
22. (i) Why is H_2O a liquid and H_2S a gas?
 (ii) Why is H_2S less acidic than H_2Te ?
23. Chlorofluorocarbons are known as freons. These are used as refrigerants and aerosol sprays. Nowadays scientists all over the world are busy in searching alternatives of freons as refrigerants.
- Now answer the following questions :
- What is the formula of freons?
 - What are the disadvantages of using freons?
 - What value is associated with this statement?

24. Account for the following :

- Xenon does not form fluorides such as XeF_3 and XeF_5 .
- Out of noble gases, only xenon is known to form established chemical compounds.

OR

Account for the following :

- OF_2 is called oxygen difluoride and not fluorine oxide.
 - Tendency to show -2 oxidation state diminishes from sulphur to polonium in group 16.
 - Interhalogen compounds are more reactive than its elemental form.
25. (i) Phosphinic acid behaves as a monoprotic acid. Why?
 (ii) What happens when phosphine reacts with copper sulphate and mercuric chloride solution?

- NF_3 is an exothermic compound but NCl_3 is an endothermic compound. Why?

26. (i) Write the conditions to maximize the yield of H_2SO_4 by contact process.
 (ii) Why is K_{a2} less than K_{a1} for H_2SO_4 in water?
27. Comment on the nature of two $\text{S} - \text{O}$ bonds formed in SO_2 molecule. Are the two $\text{S} - \text{O}$ bonds in this molecule equal?
28. (i) Which of the following does not exist and why?
 (a) XeOF_4 (b) NeF_2
 (c) XeF_4 (d) XeF_6
 (ii) How are XeO_3 and XeOF_4 prepared?
 (iii) Noble gas elements have very low melting and boiling points. Explain.
 (iv) Why is helium used in a diving apparatus?
 (v) Give the structure, type of hybridization and geometry of XeF_2 .

OR

- How would you account for the following :
 (a) Fluorine never act as the central atom in polyatomic interhalogen compounds.
 (b) The electron gain enthalpy (with negative sign) for fluorine is less than that for chlorine, still fluorine is a stronger oxidizing agent than chlorine.
 (c) ClF_3 molecule has a T-shaped structure and not a trigonal planar one.
 - With what neutral molecule is ClO^- isoelectronic? Is that molecule a Lewis base?
 - How can you prepare Cl_2 from HCl and HCl from Cl_2 ? Write reactions only.
29. (i) How many $\text{P}-\text{P}$ bonds present in cyclotrimetaphosphoric acid $(\text{HPO}_3)_3$?
 (ii) Why does a nitric acid bottle appear yellow?
 (iii) Bond angle in PH_4^+ is higher than in PH_3 . Why?
 (iv) Arrange NF_3 , PF_3 , AsF_3 , BiF_3 in increasing order of ionic character. Give reason.

- (v) Why does nitrogen show catenation property less than phosphorus?

OR

- (i) What is the covalence of nitrogen in N_2O_5 ?
 - (ii) What happens when white phosphorus is heated with concentrated NaOH solution in an inert atmosphere of CO_2 ?
 - (iii) How is nitric acid prepared in laboratory?
 - (iv) Ammonia is a stronger base than phosphine. Why?
 - (v) In the solid state, PCl_5 behaves as an ionic species. Give reason.
30. (i) OF_6 compound is not known. Give reason.
 (ii) Why does ozone act as a powerful oxidising agent?
 (iii) Why is the bond dissociation energy of fluorine molecule less than that of chlorine molecule?
 (iv) Draw the structure of O_3 molecule.
 (v) H_2S is more acidic than H_2O . Why?

OR

- (i) Sulphur disappears when boiled with sodium sulphite. Why?
- (ii) Why is HF not stored in glass bottles?
- (iii) SF_6 is much less reactive than SF_4 . Why?
- (iv) Oxygen molecule has the formula O_2 while sulphur is S_8 . Give reason.
- (v) Why is sulphurous acid a reducing agent?

SOLUTIONS

1. The bond dissociation enthalpy of multiple $N \equiv N$ bond is very high.
2. Oxygen exists as diatomic molecule having weak van der Waals' forces whereas sulphur exists as octa-atomic molecule with strong intermolecular forces.
3. HCl is stronger acid than HF. The acidic strength of hydrogen halides is $HF < HCl < HBr < HI$.
4. $XeF_6 + 2H_2O \rightarrow XeO_2F_2 + 4HF$
5. Three P—OH bonds are present in H_3PO_4 molecule. Therefore, its basicity is three.
6. The thermal stability of the hydrides of group 16 elements decrease down the group, i.e., $H_2O > H_2S > H_2Se > H_2Te$.

7. Fluorine forms only one oxoacid, HOF due to high electronegativity and small size.
8. Noble gases being monoatomic have weak dispersion forces and therefore, liquefied at very low temperatures.

9.

White phosphorus	Red phosphorus
It is a white, waxy solid, which is insoluble in water but soluble in CS_2 .	When white phosphorus is heated at 573 K changes into red phosphorus. It is insoluble in both water and CS_2 .
It glows in dark due to oxidation.	It does not glow in the dark.

10. The two examples of anomalous behaviour of fluorine are :

1. Due to non-availability of d -orbitals in its valence shell, fluorine cannot expand its octet, therefore, fluorine shows only -1 oxidation state.
2. Due to its small size, F—F bond dissociation energy is lower than that of Cl—Cl bond.

OR

- (i) $2Ca(OH)_{2(dil.)} + 2Cl_2 \rightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$
Bleaching powder
- (ii) $2Fe_{2(g)} + 2H_2O_{(l)} (hot) \rightarrow 4H_{(aq)}^+ + 4Fe_{(aq)}^- + O_{2(g)}$

11. (i) Increasing bond dissociation enthalpy order is : $I_2 < F_2 < Br_2 < Cl_2$
Bond dissociation enthalpy of F_2 is less than that of Br_2 and Cl_2 due to the lone pair - lone pair repulsion.
- (ii) Increasing acid strength order is : $HF < HCl < HBr < HI$
As the size of halogen atom increases, bond dissociation enthalpies of H—X bond decreases.
12. (i) $XeF_4 + O_2F_2 \xrightarrow{143\text{ K}} XeF_6 + O_2$
 (ii) $XeF_4 + SbF_5 \rightarrow [XeF_5]^+ [SbF_6]^-$
13. Phosphorus cannot increase its oxidation number beyond +5 since there are only five

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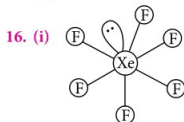
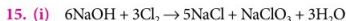
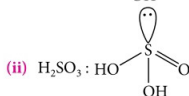
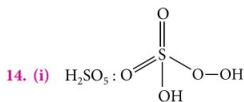
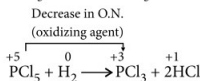
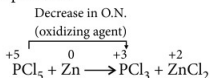
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electrons in its valence shell. Hence, it cannot act as a reducing agent.

Examples are :

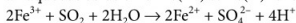


(ii) No, the products of hydrolysis are XeOF_4 and XeO_2F_2 where the oxidation states of all the elements remain the same as it was in the reacting state.

17. (i) As electronegativity decreases down the group, electron density and repulsive interactions between electron pairs also decreases. Consequently, the H-M-H bond angle decreases down the group.

(ii) On moving from NH_3 to BiH_3 , the size of the central atom increases and the electron density decreases. So, the basic strength also decreases.

18. SO_2 acts as a reducing agent and hence reduces an aqueous solution of Fe(III) to Fe(II) ions.



19. (i) Noble gases are mostly inert because of the following reasons :

- They have completely filled ns^2np^6 electronic configurations in their valence shells.
- Electron gain enthalpies of noble gases are positive.
- They have high ionization enthalpies.

(ii) Neon lights are visible from long distances even in fog and mist and hence, neon is generally used for warning signals.

(iii) In a period, it is observed that atomic radius decreases as the atomic number increases from 1st group to 17th group. However, the radii values of noble gases which come after the elements of group 17th are exceptionally high. This is due to the fact that in the case of noble gases, the atomic radii correspond to van der Waals' radii which are always larger than covalent radii. van der Waals' radii of noble gases increase gradually from He to Rn. This is due to addition of new energy shell from member to member.

20. (i) ICl_4^-
(Number of valence electrons
 $= 7 + (4 \times 7) + 1 = 36$)

It is sp^3d^2 -hybridized, square planar in shape and isoelectronic with XeF_4 .

(ii) IBr_2^-
(Number of valence electrons
 $= 7 + (2 \times 7) + 1 = 22$)

It is sp^3d -hybridized, linear in shape and isoelectronic with XeF_2 .

(iii) BrO_3^-
(Number of valence electrons
 $= 7 + 3 \times 6 + 1 = 26$)

It is sp^3 -hybridized, trigonal pyramidal in shape and isoelectronic with XeO_3 .

21. (i) $\text{R}_3\text{N}=\text{O}$ molecule has five covalent bonds with N-atom. The octet in N cannot be extended as it does not have d -orbitals for formation of $p\pi-d\pi$ bond. Whereas P can extend its octet since it has d -orbitals in its valence shell and form $p\pi-d\pi$ bond. Hence, $\text{R}_3\text{P}=\text{O}$ can exist.

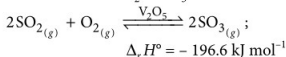
- (ii) Among hydrides of group-15 elements, the bond length increases from N – H to Bi – H with increasing size of element. Bi – H bond is largest and weakest, it can break more easily and evolve H_2 gas which acts as the reducing agent.
22. (i) Due to greater electronegativity of O than S, H_2O undergoes extensive intermolecular H-bonding. As a result, H_2O exists as an associated molecule in which each H_2O is tetrahedrally surrounded by four water molecules. Quite a large amount of energy is required to break these hydrogen bonds. Therefore, H_2O is a liquid at room temperature. The hydrogen bonding is absent in H_2S , hence, the molecules are unassociated. Hence, H_2S exists in gaseous state.
- (ii) Due to decrease in bond ($E-H$) dissociation enthalpy down the group, acidic character increases.
Hence H_2S is less acidic than H_2Te .
23. (i) Freons are CF_2Cl_2 , $CFCl_3$ etc.
- (ii) Freons are very stable compounds. They rise up in the atmosphere undecomposed and responsible for depletion of ozone layer. Ozone layer depletion causes many harmful effects on life.
- (iii) We must think about environmental protection.
24. (i) All the filled orbitals of Xe have paired electrons. The promotion of one, two or three electrons from the $5p$ -filled orbitals to the $5d$ -vacant orbitals will give rise to two, four and six half-filled orbitals. So Xe can combine with even but not odd number of F atoms. Hence, it cannot form XeF_3 and XeF_5 .
- (ii) Except radon which is radioactive, Xe has least ionization energy among noble gases and hence, it readily forms chemical compounds particularly with O_2 and F_2 .

OR

- (i) As fluorine is more electronegative than oxygen so, compound of oxygen and fluorine are called oxygen fluorides and not fluorine oxides.

- (ii) From sulphur to polonium electronegativity decreases hence tendency to show negative oxidation state decreases.
- (iii) Since $X-X$ bond between two dissimilar electronegative elements is weaker than two similar elements (except F – F). Hence, interhalogen compounds have low bond dissociation energy and correspondingly it is more reactive than its elemental form.
25. (i) Phosphinic acid, H_3PO_2 has one P – OH group and two hydrogen directly attached to phosphorous. It has only one ionisable hydrogen and hence behaves as a monoprotic acid.
- (ii) When phosphine reacts with copper sulphate and mercuric chloride solution, the corresponding phosphides are obtained.
- $$\begin{array}{rcl}
 3CuSO_4 + 2PH_3 & \rightarrow & Cu_3P_2 + 3H_2SO_4 \\
 \text{Copper sulphate} & & \text{Copper phosphide} \\
 3HgCl_2 + 2PH_3 & \rightarrow & Hg_3P_2 + 6HCl \\
 \text{Mercuric chloride} & & \text{Mercuric phosphide}
 \end{array}$$
- (iii) Bond strength of N – F bond is more than that of N – Cl bond.

26. (i) The key step in the production of H_2SO_4 is the oxidation of SO_2 to SO_3 .



The reaction is exothermic, reversible and the forward reaction proceeds with decrease in volume. Therefore, in accordance with Le Chatelier's principle, low temperature (720 K), high pressure (2 bar) and use of V_2O_5 as a catalyst to increase the rate at 720 K are the favourable conditions for maximum yield.

- (ii) K_{a2} is less than K_{a1} because the negatively charged HSO_4^- ion has much less tendency to donate a proton to H_2O as compared to neutral H_2SO_4 .
27. In SO_2 , S is sp^2 -hybridized. Two $\ddot{O}=\ddot{S}=\ddot{O}:$ \longleftrightarrow $:\ddot{O}=\ddot{S}=\ddot{O}:$ of the three sp^2 -orbitals form two σ -bonds while the third contains the lone pair of electrons. S is now left with one half-filled p -orbital and one half-filled d -orbital. These form one $p\pi-p\pi$ and

one $p\pi - d\pi$ double bond with oxygen atom. Thus, SO_2 has bent structure with $\text{O} - \text{S} - \text{O}$ bond angle of 119.5° . Due to resonance, the two π -bonds are equal (143 pm).

28. (i) The sum of first and second ionization enthalpies of Ne are much higher than those of Xe. Thus, F_2 can oxidise Xe to Xe^{2+} but cannot oxidise Ne to Ne^{2+} . In other words, NeF_2 does not exist and all the xenon fluorides (XeF_4 and XeF_6) and xenon oxyfluoride (XeOF_4) do exist.

- (ii) Hydrolysis of XeF_4 and XeF_6 with water give XeO_3 .

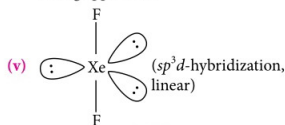


In contrast, partial hydrolysis of XeF_6 gives XeOF_4 .



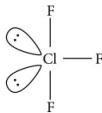
- (iii) Noble gas elements exist as monatomic gases and the only attractive forces in them are the weak van der Waals' forces, and therefore, they are liquefied at very low temperatures. As a result, they have very low melting and boiling points.

- (iv) Unlike nitrogen (the main constituent of air), helium is not soluble in blood even under high pressure. Due to this reason, the mixture of helium and oxygen is safer for respiration and therefore, it is used in a diving apparatus.



OR

- (i) (a) Fluorine being smaller in size and highly electronegative cannot show higher valence state.
 (b) It is due to low enthalpy of dissociation of $\text{F}-\text{F}$ bond and high hydration enthalpy of F^- .
 (c) ClF_3 has sp^3d hybridization. The axial fluorine atoms will be bent towards the equatorial



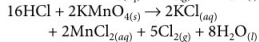
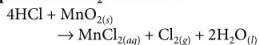
fluorine in order to minimise the lone pair-lone pair repulsions. The shape would be that of a slightly bent T-shaped.

- (ii) Number of electrons in ClO^- is $= 17 + 8 + 1 = 26$. An isoelectronic neutral molecule is OF_2 molecule ($8 + 9 + 9 = 26$ electrons.)

It can act as a very weak Lewis base.

Since electronegativity of fluorine is very high, the non-bonding electron pairs on oxygen would be pulled towards fluorine making them less available for it to act as Lewis base.

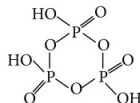
- (iii) Preparation of Cl_2 from HCl :



Preparation of HCl from Cl_2 :

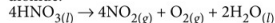


29. (i) The structure of $(\text{HPO}_3)_3$ is



Number of $\text{P}-\text{P}$ bonds = Zero.

- (ii) The yellow colour of the concentrated nitric acid bottle is due to the partial decomposition of the HNO_3 to nitrogen dioxide.



- (iii) In both PH_4^+ and PH_3 , P has sp^3 hybridized. PH_4^+ contains all the four bond pairs so its bond angle is $109^\circ 28'$ as expected for tetrahedral geometry. PH_3 contains three bond pairs and one lone pair. Lone pair repels the bond pair and decreases its bond angle to 93.6° .

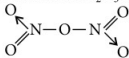
- (iv) $\text{NF}_3 < \text{PF}_3 < \text{AsF}_3 < \text{BiF}_3$

For same anion if size of cation increases the tendency of polarisation decreases and correspondingly ionic character also increases.

- (v) The single N—N bond is weaker than the single P—P bond because of high interelectronic repulsion of the non-bonding electrons, owing to the small bond length. As a result the catenation tendency is weaker in nitrogen.

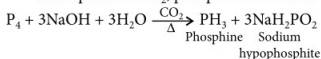
OR

- (i) The structure of N_2O_5 is

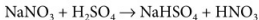


From the structure of N_2O_5 , it is evident that covalence of nitrogen is four.

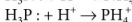
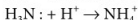
- (iii) When white phosphorus is heated with concentrated NaOH solution in an inert atmosphere of CO_2 , phosphine is formed.



- (iii) Nitric acid in laboratory is prepared by heating $NaNO_3$ and conc. H_2SO_4 in a glass retort.



- (iv) Due to the presence of lone pairs of electrons on the central atom both NH_3 and PH_3 are Lewis bases. When NH_3 or PH_3 accept a proton, an additional N—H or P—H bond is formed.

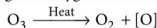


Due to smaller size of N than P, N—H bond thus formed is much stronger than P—H bond. As a result NH_3 has more tendency than PH_3 to accept a proton. Therefore, NH_3 is stronger base than PH_3 .

- (v) PCl_5 is ionic in the solid state because it exists as $[PCl_4]^+ [PCl_6]^-$ in which the cation is tetrahedral and anion is octahedral.

30. (i) Due to small size of O, six F-atoms cannot be accommodated around oxygen atom. Hence, OF_6 is not known or oxygen can not expand its valency beyond 4 due to absence of *d*-orbital.

- (ii) On heating, ozone readily decomposes to give dioxygen and nascent oxygen.



Nascent oxygen

Since nascent oxygen is very reactive, therefore, O_3 acts as a powerful oxidising agent.

- (iii) Lower value of bond dissociation energy of F_2 is due to the strong repulsion between the non-bonding electrons of F-atoms in the small sized F_2 molecule.

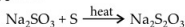
- (iv) Structure of ozone :



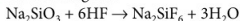
- (v) The size of central atom in H_2S is larger than that in H_2O . S—H bond is larger and weaker than O—H bond. Hence, H_2S is more acidic than H_2O .

OR

- (i) When sodium sulphite is heated with sulphur, we get sodium thiosulphate which is soluble in water that is why sulphur disappears.



- (ii) HF attacks glass.



- (iii) In SF_6 , six F-atoms protect the sulphur atom from attack by the reagent to such an extent that even thermodynamically most favourable reactions like hydrolysis do not occur. But in SF_4 , S is not sterically protected since it is surrounded by only four F-atoms. Hence, SF_4 is reactive.

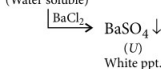
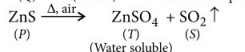
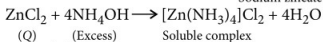
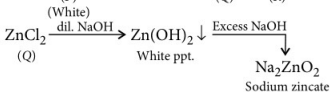
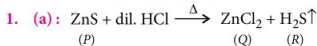
- (iv) Due to small size oxygen forms $p\pi-p\pi$ multiple bonds. As a result oxygen exist as diatomic (O_2) molecule. Due to its bigger size sulphur does not forms $p\pi-p\pi$ multiple bonds. Consequently, sulphur because of its higher tendency of catenation and lower tendency for $p\pi-p\pi$ multiple bonds forms octa-atomic (S_8) molecules having eight-membered puckered ring structure.

- (v) On the basis of electronic configuration of S ($3s^2 3p^4$), the maximum oxidation state possible for S is + 6. In H_2SO_3 , the oxidation state of S is + 4, by acting as a reducing agent, it can increase its oxidation state to + 6. So, it acts as a reducing agent.

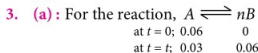


CHEMISTRY MUSING

SOLUTION SET 13



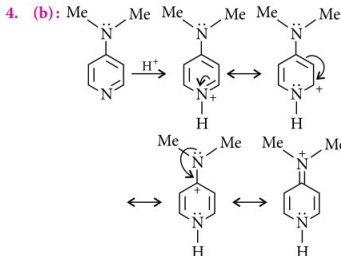
2. (b)



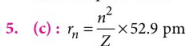
It is clear that amount of B formed is twice that of A. Then, $n = \frac{0.06}{0.03} = 2$

Now, for the reaction, $A \rightleftharpoons 2B$

$$K_c = \frac{[B]^2}{[A]} = \frac{[0.06]^2}{[0.03]} = 0.12$$



The conjugate acid is stabilised by resonance with complete octet.



Here, $n = 1$ and $Z = 1$ for H, $Z = 2$ for He and $Z = 3$ for Li

$$r_H = \frac{1^2}{1} \times 52.9 \text{ pm} = 52.9 \text{ pm}$$

$$r_{\text{He}^+} = \frac{1^2}{2} \times 52.9 \text{ pm} = 26.45 \text{ pm}$$

$$r_{\text{Li}^{2+}} = \frac{1^2}{3} \times 52.9 \text{ pm} = 17.63 \text{ pm}$$

Thus, the order is $r_H > r_{\text{He}^+} > r_{\text{Li}^{2+}}$

6. (a): Hyperconjugation and inductive effects increase the stability of carbocation. The correct order of stability of carbocations is $3^\circ > 2^\circ > 1^\circ$. Thus, (iii) > (v) > (iv) > (ii) > (i) (i) and (ii) are destabilized by the $-I$ effect of CCl_3 and Cl groups, (iv) is also destabilised by $-I$ effect but the effect is less pronounced as CCl_3 group is present at β -position.

7. (b): KF is a fluoride ion donor, hence it reacts with XeF_6 to give a fluoro anion.



8. (b): $\text{XeF}_6 + 3\text{H}_2\text{O} \longrightarrow \text{XeO}_3 + 6\text{HF}$
 (A) (B)

XeO_3 has trigonal pyramidal shape.

9. (1): No. of moles in 1st experiment

$$= 0.2 \text{ mol L}^{-1} \times \frac{500}{1000} \text{ L} = 0.1 \text{ mol}$$

No. of moles in 2nd experiment

$$= 0.2 \text{ mol L}^{-1} \times \frac{250}{1000} \text{ L} = 0.05 \text{ mol}$$

Heat of neutralization for strong acid and base
 $= -57 \text{ kJ mol}^{-1}$

Heat released (q_1) in the 1st experiment

$$= 0.1 \times -57 = -5.7 \text{ kJ}$$

and heat released (q_2) in the 2nd experiment

$$= 0.05 \times -57 = -2.85 \text{ kJ}$$

i.e., $q_1 = 2q_2$ but $q = ms\Delta t$

$$m_1 = (500 + 500) \times 1 \text{ g/cm}^3 = 1000 \text{ g}$$

$$m_2 = (250 + 250) \times 1 \text{ g/cm}^3 = 500 \text{ g}$$

$$\text{and } t = \frac{q}{m \times s} \therefore t_1 = \frac{5.7}{1000 \times s} \text{ and } t_2 = \frac{2.85}{500 \times s}$$

$$\text{So, } t_1/t_2 = \frac{5.7}{1000 \times s} \times \frac{500 \times s}{2.85} = 1$$

10. (2):

	Sample-1	Sample-2
Concentration :	0.4	0.1
$t_{1/2}$:	50	200

This implies $t_{1/2} \propto \frac{1}{a}$

If $n = 2$ then $t_{1/2} \propto \frac{1}{a}$

$$\left(\therefore t_{1/2} \propto \frac{1}{a^{n-1}} \right)$$





EXAMINER'S MIND NCERT CLASS XII

The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XII. This year JEE (Main & Advanced) / AIPT / AIIMS / other PMTs have drawn their papers heavily from NCERT books.

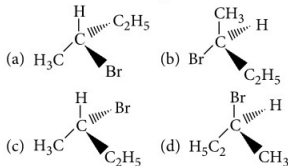
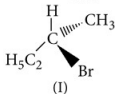
GENERAL PRINCIPLES AND PROCESSES OF ISOLATION OF ELEMENTS | COORDINATION COMPOUNDS | HALOALKANES AND HALOARENES

SECTION - I

Only One Option Correct Type

This section contains 20 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

- Thermite is a mixture of
(a) $\text{Zn} + \text{Mg}$ (b) $\text{Fe} + \text{Al}$
(c) $\text{Fe}_2\text{O}_3 + \text{Al}$ (d) $\text{Cu} + \text{Mg}$
- When 0.1 mol of $\text{CoCl}_3(\text{NH}_3)_5$ is treated with excess of AgNO_3 , 0.2 mol of AgCl is obtained. The conductivity of solution will correspond to
(a) 1 : 3 electrolyte (b) 1 : 2 electrolyte
(c) 1 : 1 electrolyte (d) 3 : 1 electrolyte.
- Which of the following structures is enantiomeric with the molecule (I) given below :

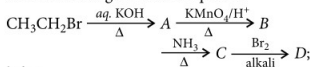


- During a column chromatography, a mixture of components A, B and C is passed through Al_2O_3 column. On adding eluant, compound

'A' is eluted first then 'B' and in the end 'C'. Which of the following statements regarding the components is correct?

- The order of adsorption of A, B and C is $C > B > A$.
 - The order of adsorption of A, B and C is $A > B > C$.
 - The order of adsorption of A, B and C is $B > A > C$.
 - The order of adsorption of A, B and C is $B > C > A$.
- Which one of the following aqua complexes will exhibit the minimum paramagnetic behaviour?
(a) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ (b) $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$
(c) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ (d) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
(At. No. Cr = 24, Mn = 25, Fe = 26, Ni = 28)

- In the following reactions sequence

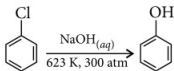


'D' is

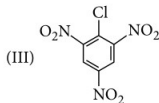
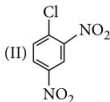
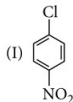
- CH_3Br
 - CH_3CONH_2
 - CH_3NH_2
 - CHBr_3
- In a mixture of PbS , ZnS and FeS , each component is separated from other by using the reagents in the following sequence in froth floatation process
(a) potassium ethyl xanthate, KCN
(b) potassium ethyl xanthate, KCN, NaOH, CuSO_4 , acid
(c) KCN, CuSO_4 , acid
(d) none of the above.

8. Which kind of isomerism is exhibited by $[\text{Co}(\text{NH}_3)_4\text{Br}_2]\text{Cl}$?
- Geometrical and ionisation
 - Geometrical and optical
 - Optical and ionisation
 - Geometrical only

9. Chlorobenzene can be converted into phenol by heating in aqueous sodium hydroxide solution at a temperature of 623 K and a pressure of 300 atm.



However the rate of reaction can be increased by presence of certain groups in benzene ring. What will be the order of reactivity of following compounds towards the above substitution reaction?



- (III) > (II) > (I)
 - (II) > (III) > (I)
 - (I) > (II) > (III)
 - (I) > (III) > (II)
10. Duralumin is used in aircraft industry for its light weight and high strength. It is an alloy of
- Al, Cu, Mg and Mn
 - Al, Zn, Fe and Sn
 - Al, Ti, Ce and Fe
 - Al, Fe, Zn and Sn.
11. *Fac-mer* isomerism is associated with which one of the following complexes?
- $[\text{M}(\text{AA})_2]$
 - $[\text{MA}_3\text{B}_3]$
 - $[\text{M}(\text{AA})_3]$
 - $[\text{MABCD}]$
12. Positive iodoform test is given by
- formaldehyde
 - acetophenone
 - benzophenone
 - all of these.

13. The process of leaching in case of low grade copper ores is carried out
- with NaOH and O_2
 - with NaCN
 - with acids in presence of O_2 .
 - by boiling the ore with water.

14. Which of the following complex compounds will exhibit highest paramagnetic behaviour?
- $[\text{Ti}(\text{NH}_3)_6]^{3+}$
 - $[\text{Cr}(\text{NH}_3)_6]^{3+}$
 - $[\text{Co}(\text{NH}_3)_6]^{3+}$
 - $[\text{Zn}(\text{NH}_3)_6]^{2+}$
- (At. No. Ti = 22, Cr = 24, Co = 27, Zn = 30)

15. Classify the following compounds as primary, secondary and tertiary halides.

- 1-Bromobut-2-ene
 - 4-Bromopent-2-ene
 - 2-Bromo-2-methylpropane
- (i) secondary, (ii) tertiary, (iii) primary
 - (i) secondary, (ii) primary, (iii) tertiary
 - (i) primary, (ii) tertiary, (iii) secondary
 - (i) primary, (ii) secondary, (iii) tertiary

16. If an impurity in a metal has a greater affinity for oxygen and is more easily oxidised than the metal, then the purification of metal may be carried out by

- poling
- zone refining
- electrolytic refining
- cupellation

17. The correct IUPAC name of the compound $[\text{Cr}(\text{NH}_3)_5(\text{NCS})][\text{ZnCl}_4]$, is

- pentaammineisothiocyanatochromium(III) tetrachloridozincate(II)
- pentaammineisothiocyanatozinc chloridochromate(III)
- pentaammineisothiocyanatochromate(II)
- isothiocyanatopentaamminechromium(II) zincchlorido(IV).

18. *o*-Chlorotoluene can undergo
- electrophilic aromatic substitution
 - nucleophilic aromatic substitution
 - nucleophilic aliphatic substitution
 - free radical substitution
- only (i)
 - (i) and (iv)
 - (i), (ii) and (iv)
 - all the four.

19. In the extraction of aluminium from bauxite, cryolite is used to
- decrease the boiling point of aluminium
 - purify the bauxite
 - make the mass lighter
 - decrease melting point of alumina and increase conductivity.
20. Which of the following statement(s) is/are correct?
- In octahedral complexes, t_{2g} orbitals possess low energy as compared to e_g orbitals.
 - In tetrahedral complexes, t_{2g} orbitals possess high energy as compared to e_g orbitals.
 - In octahedral complexes, e_g orbitals possess low energy as compared to t_{2g} orbitals.
- (ii) only
 - (iii) only
 - (i) and (ii)
 - (i) and (iii)

SECTION - II

One or More Options Correct Type

This section contains 5 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONE or MORE are correct.

21. Which of the following products are obtained during the reaction?
- $$\text{Me}_3\text{CCH}_2\text{OH} \xrightarrow{\text{HBr}}$$
- $\text{Me}_3\text{CCH}_2\text{Br}$
 - $\text{Me}_2\text{CBrCH}_2\text{CH}_3$
 - $\text{Me}_3\text{CCH}_2\text{CH}_2\text{CMe}_3$
 - Me_3CCHO
22. NaCN is sometimes added in froth floatation process with ZnS and PbS minerals because
- Pb(CN)_2 is precipitated while there is no effect on ZnS
 - ZnS forms soluble complex while PbS forms froth
 - It acts as a depressant
 - NaCN is never added in froth floatation process.
23. Mn^{2+} forms different complexes with Br^- ions having magnetic moment value 5.92 BM. The correct formula and geometry of the complex, is

- $[\text{MnBr}_4]^{2-}$; tetrahedral
- $[\text{MnBr}_4]^{2-}$; square planar
- $[\text{MnBr}_6]^{4-}$; octahedral
- $[\text{MnBr}_5]^{3-}$; trigonal planar.

24. Isobutene will be obtained on treatment of which of the following compounds by alcoholic KOH?

- $(\text{CH}_3)_3\text{CCl}$
- $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{Cl}$
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$
- $\text{CH}_3-\underset{\text{Cl}}{\text{CH}}-\text{CH}_2\text{CH}_3$

25. Which of the following involves dsp^2 hybridisation and are square planar?

- $[\text{Cu(CN)}_4]^{3-}$
- $[\text{Cu(NH}_3)_4]^{2+}$
- $[\text{Ni(CN)}_4]^{2-}$
- $[\text{Cr(NH}_3)_6]^{3+}$

SECTION - III

Paragraph Type

This section contains 2 paragraphs each describing theory, experiment, data, etc. Six questions relate to two paragraphs with three questions on each paragraph. Each question of a paragraph has only one correct answer among the four choices (a), (b), (c) and (d).

Paragraph for Questions 26 to 28

According to valence bond theory, the metal atom or ion under the influence of ligands can use its $(n-1)d$, ns , np or ns , np , nd orbitals for hybridisation to yield a set of equivalent orbitals of definite geometry such as octahedral, tetrahedral, square planar and so on. These hybridised orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.

26. Which of the following compounds is square planar and does not have any unpaired electron?
- Ni(CO)_4
 - $[\text{Ni(H}_2\text{O)}_6]^{2+}$
 - $[\text{NiCl}_4]^{2-}$
 - $[\text{Ni(CN)}_4]^{2-}$
27. $[\text{CoF}_6]^{3-}$ is
- paramagnetic and undergoes sp^3d^2 hybridisation
 - diamagnetic and undergoes d^2sp^3 hybridisation

- (c) paramagnetic and undergoes sp^3d hybridisation
 (d) diamagnetic and undergoes sp^3 hybridisation.

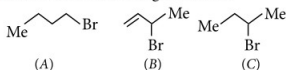
28. Which of the following descriptions about $[\text{FeCl}_6]^{4-}$ is correct?

- (a) ds^3 , inner orbital complex, diamagnetic
 (b) sp^3d^2 , outer orbital complex, paramagnetic
 (c) d^2sp^3 , inner orbital complex, paramagnetic
 (d) sp^3d^2 , outer orbital complex, diamagnetic

Paragraph for Questions 29 to 31

In nucleophilic substitution reaction, a nucleophile reacts with haloalkane (the substrate) having a partial positive charge on the carbon atom bonded to halogen. A substitution reaction takes place and halogen atom, called leaving group departs as halide ion. Since the substitution reaction is initiated by a nucleophile, it is called nucleophilic substitution reaction.

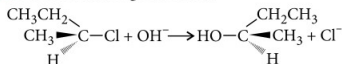
29. Consider the following bromides :



The correct order of S_N1 reactivity is

- (a) $A > B > C$ (b) $B > C > A$
 (c) $B > A > C$ (d) $C > B > A$

30. In the reaction given below :



Which of the following statements is correct?

- (a) The reaction proceeds via S_N2 mechanism hence inversion of configuration takes place.
 (b) The reaction proceeds via S_N1 mechanism hence inversion of configuration takes place.
 (c) The reaction proceeds via S_N2 mechanism hence there is no change in the configuration.
 (d) The reaction proceeds via S_N1 mechanism hence there is no change in the configuration.

31. The order of reactivity of various alkyl halides towards nucleophilic substitution follows the order

- (a) $R-I > R-Br > R-Cl > R-F$
 (b) $R-F > R-Cl > R-Br > R-I$
 (c) $R-Cl > R-Br > R-I > R-F$
 (d) $R-Br > R-I > R-Cl > R-F$

SECTION - IV

Matching List Type

This section contains 3 multiple choice questions. Each question has matching lists. The codes for the lists have choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

32. Match the List I with List II and select the correct answer using the code given below the lists :

List I

(Element)

- P. Cu 1. Direct reduction of sulphide by heating
 Q. Sn 2. Electrolysis of fused chloride and fluoride
 R. Hg 3. Partial oxidation of sulphide ore
 S. Ca 4. Reduction of oxide with carbon

List II

(Method of extraction)

- P Q R S
 (a) 3 1 2 4
 (b) 3 4 1 2
 (c) 1 3 2 4
 (d) 4 1 2 3

33. Match the List I with List II and select the correct answer using the code given below the lists :

List I

- P. $[\text{Fe}(\text{CN})_6]^{3-}$
 Q. $[\text{CoF}_6]^{3-}$
 R. $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$
 S. $[\text{Co}(\text{NH}_3)_6]^{3+}$

List II

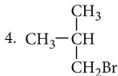
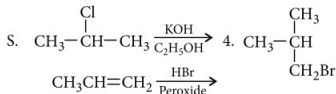
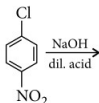
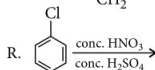
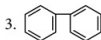
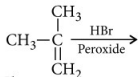
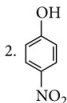
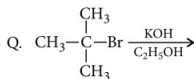
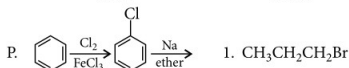
1. Zero
 2. 5.92 B.M.
 3. 4.89 B.M.
 4. 1.732 B.M.

- P Q R S
 (a) 2 3 4 1
 (b) 3 2 1 4
 (c) 1 3 4 2
 (d) 4 3 2 1

34. Match the List I with List II and select the correct answer using the code given below the lists :

List I

List II



	P	Q	R	S
(a)	4	2	1	3
(b)	3	4	2	1
(c)	2	1	3	4
(d)	1	3	4	2

SECTION - V

Assertion-Reason Type

In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
 (b) If both assertion and reason are true but reason is not the correct explanation of assertion.
 (c) If assertion is true but reason is false.
 (d) If both assertion and reason are false.
35. **Assertion** : Roasting is a process in which the ore is heated strongly in absence of air.
Reason : Concentration of sulphide ore is done by calcination.
36. **Assertion** : Tetrahedral complexes having two different types of unidentate ligands coordinated with central metal ion will show geometrical isomerism.
Reason : Geometrical isomerism arises in homoleptic complexes due to different possible geometric arrangements of the ligands.
37. **Assertion** : Aryl halides are highly reactive towards nucleophilic substitution reactions.
Reason : In case of haloarenes, halogen atom is attached to sp hybridised carbon atom.
38. **Assertion** : Chromatography in general involves a mobile phase (a gas, a liquid or a supercritical fluid) and a stationary phase (like Al_2O_3 column).
Reason : A component which is less soluble in stationary phase takes longer time to travel through it than the component which is more soluble in stationary phase.
39. **Assertion** : $\text{K}_2[\text{Ni}(\text{EDTA})]$ is more stable than $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$.
Reason : Ni is a transition element while Al is a non-transition element.
40. **Assertion** : $\text{S}_{\text{N}}2$ reaction proceeds with racemisation while $\text{S}_{\text{N}}1$ reaction proceeds with complete stereochemical inversion.
Reason : $\text{S}_{\text{N}}2$ is two steps reaction while $\text{S}_{\text{N}}1$ is one step reaction.

SECTION - VI

Integer Value Correct Type

This section contains 10 questions. The answer to each question is a single digit integer, ranging from 0 to 9 (both inclusive).

41. The number of metals produced by reduction of their oxides with carbon, hydrogen or a more active metal among the following is Fe, Li, Au, Cu, Na, Pt, Cr, Ag, Hg, V, Mn, Mg
42. The total isomers formed by $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Br}$ are

43. Total number of possible monochloro structural isomers expected to be formed by free radical monochlorination of $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$ is
44. The total number of oxide ores among the following ores is
Carnallite, Bauxite, Magnetite, Haematite, Cuprite, Copper pyrites, Galena and Cassiterite.
45. No. of unpaired electrons present in $[\text{Co}(\text{NH}_3)_6]^{3+}$ is
46. Among the following, number of reagents required to distinguish chlorobenzene from chlorocyclohexane is
 $\text{AgNO}_3/\text{C}_2\text{H}_5\text{OH}$, Br_2/CCl_4 , $[\text{Ag}(\text{NH}_3)_2]\text{OH}$, AgCN/HNO_3 , Na fusion/ AgNO_3
47. Oxidation state of cobalt in the compound $[\text{Co}_2(\text{CO})_8]$ is
48. The value of CFSE for $[\text{Ti}(\text{H}_2\text{O})_6]^{2+}$ complex is $n \times 10^{-1} \Delta_o$. The value of n will be
49. Given

$$\text{C}_3\text{H}_7\text{I} \xrightarrow[\text{(alc.)}]{\text{KOH}} \text{X} \xrightarrow[\Delta]{\text{NBS, } h\nu} \text{Y} \xrightarrow[\text{(alc.)}]{\text{KCN}} \text{Z} \xrightarrow{\text{Br}_2} \text{Z}'$$
 No. of carbon atoms in the product Z' is
50. A hydrocarbon (X) having molecular weight 70 gives a single monochloride but three dichlorides on chlorination in the presence of ultraviolet light. The number of C-atoms in hydrocarbon (X) are

SOLUTIONS

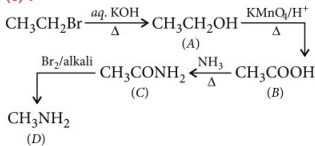
1. (c) : Thermite is a mixture of Fe_2O_3 and Al in the ratio 3 : 1. Thermite reaction involves the displacement of a metal from its oxide by more electropositive metal releasing large amount of energy.

$$\text{Fe}_2\text{O}_{3(s)} + 2\text{Al}_{(s)} \rightarrow 2\text{Fe}_{(l)} + \text{Al}_2\text{O}_{3(s)}$$
2. (b) : 0.2 mol of AgCl is obtained when 0.1 mol of $\text{CoCl}_3(\text{NH}_3)_5$ is treated with excess of AgNO_3 which shows that one molecule of the complex gives two Cl^- ions in solution. Thus, the formula of the complex is $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ i.e., 1 : 2 electrolyte.
3. (a) : Compound (a) is enantiomer of compound (I) because the configuration of two groups, i.e., CH_3 and C_2H_5 in them is reversed at the chiral carbon.

4. (a) : Since compound 'A' comes out before 'B', 'B' is more readily adsorbed than 'A' and 'B' comes out before 'C', hence 'C' is more readily adsorbed than 'B'. Hence, the order of adsorption is $\text{C} > \text{B} > \text{A}$.

5. (b) : Greater the number of unpaired electrons, higher is the paramagnetism. Ni^{2+} will exhibit the minimum paramagnetic behaviour.

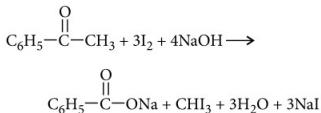
6. (c) :



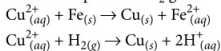
7. (b) 8. (a)
9. (a) : The presence of an electron withdrawing group ($-\text{NO}_2$) at *ortho* and *para*-positions increases the reactivity of haloarenes towards nucleophilic substitution reaction.

10. (a) 11. (b)

12. (b) : Acetaldehyde, acetone, methyl ketones containing $-\text{COCH}_3$ group and alcohol possessing CH_3CHOH group undergo haloform reaction.

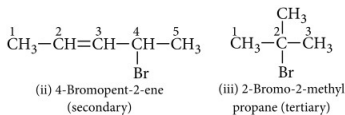


13. (c) : Leaching of low grade copper ores is carried out with an acid or bacteria, when copper goes into solution as Cu^{2+} ions. The solution containing Cu^{2+} ions is then treated with scrap iron or H_2 gas.



14. (b)

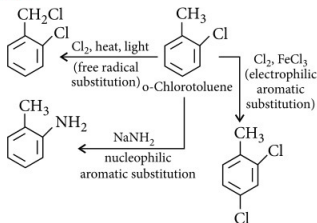
15. (d) : $\text{CH}_3\text{CH}=\text{CH}-\text{CH}_2\text{Br}$,
 (i) 1-Bromobut-2-ene (primary)



16. (d) : Cupellation can be used in such a case.

17. (a) : Pentaammineisothiocyanatochromium(III) tetrachloridozincate(II).

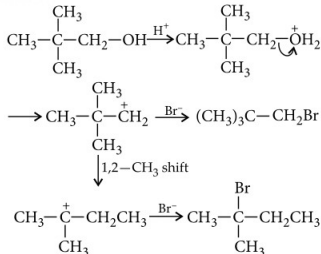
18. (c) :



19. (d) : In the extraction of aluminium from bauxite, cryolite (Na_3AlF_6) is used to decrease the melting point of alumina and to make alumina good conductor for the passage of electricity as the pure alumina is poor conductor.

20. (c) : In octahedral complexes, t_{2g} orbitals possess lower energy as compared to e_g orbitals while in tetrahedral complexes t_{2g} orbitals possess higher energy as compared to e_g orbitals.

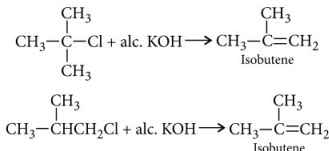
21. (a, b) :



22. (b, c) : NaCN acts as a depressant when ZnS and PbS are present in the mineral. ZnS forms soluble complex $\text{Na}_2[\text{Zn}(\text{CN})_4]$ and PbS forms froth.

23. (a, c)

24. (a, b) :

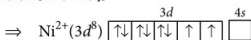


(c) and (d) would not yield isobutene.

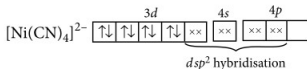
(c) yields but-1-ene and (d) yields but-2-ene.

25. (b, c)

26. (d) : $[\text{Ni}(\text{CN})_4]^{2-}$



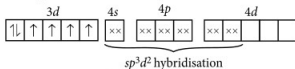
As CN^- is a strong field ligand,



Therefore, hybridisation is dsp^2 , structure is square planar and it is diamagnetic.

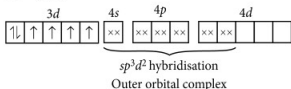
27. (a) : $[\text{CoF}_6]^{3-}$ is paramagnetic.

$[\text{CoF}_6]^{3-} : \text{Co}^{3+} (3d^6)$



28. (b) : In $[\text{FeCl}_6]^{4-}$,

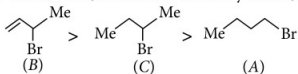
$\text{Fe}^{2+} (3d^6)$



Paramagnetic due to presence of four unpaired electrons.

29. (b) : $\text{S}_{\text{N}}1$ reaction rate depends upon the stability of the carbocation, as carbocation formation is the rate determining step. Compound (B), forms a 2° allylic carbocation which is the most stable,

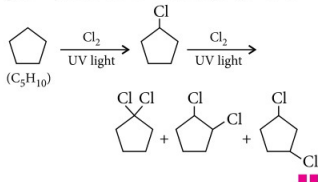
the next stable carbocation is formed from (C), it is a 2° carbocation, (A) forms the least stable 1° carbocation, the order of reactivity is thus,



- 30. (a) :** Inversion of configuration takes place via S_N2 mechanism.
- 31. (a) :** The alkyl halides are very reactive due to highly polarised C–X bond with a large difference in electronegativities of carbon and halogen atoms. The order of reactivity is iodides > bromides > chlorides > fluorides
- 32. (b)**
- 33. (d)**
- 34. (b)**
- 35. (d) :** Roasting is a process in which the ore is heated in presence of air. Sulphide ores are concentrated mainly by froth floatation process.
- 36. (d) :** Tetrahedral complexes do not show geometrical isomerism because relative positions of the unidentate ligands attached to the central metal atom are same with respect to each other. This type of isomerism arises in heteroleptic complexes.
- 37. (d) :** Aryl halides are less reactive towards nucleophilic substitution reactions as C—X bond acquires a partial double bond character due to resonance. Also halogen atom is attached to sp^2 hybridised carbon atom.
- 38. (c) :** A component which is quite soluble in the stationary phase, takes longer time to travel through it than a component which is not very soluble in the stationary phase but very soluble in the mobile phase.
- 39. (b) :** Greater stability of $K_2[Ni(EDTA)]$ is due to greater number of chelate rings formed by EDTA as compared to $C_2O_4^{2-}$.
- 40. (d) :** S_N2 reaction proceeds with complete stereochemical inversion while S_N1 reaction proceeds with racemisation. S_N2 reaction is one step in which incoming nucleophile attacks from the side opposite to that of outgoing leaving group and hence inversion of configuration occurs.

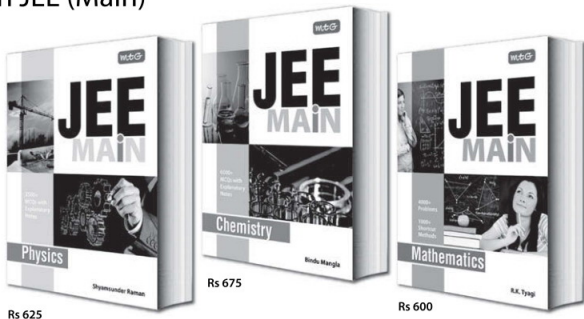
S_N1 is a two steps reaction in which carbocation is formed as intermediate and nucleophile can attack from either side resulting in racemisation.

47. (4) : Fe, Cr, V and Mn.
42. (4) : The complex $[Co(en)_2Cl_2]Br$ forms total four isomers—one is its ionisation isomer $[Co(en)_2ClBr]Cl$, *cis* isomer (which exists in two optical isomers, dextro and laevo) and *trans* isomer.
43. (4)
44. (5)
45. (0)
46. (1) : Only $AgNO_3/C_2H_5OH$ is used to distinguish chlorobenzene from chlorocyclohexane.
47. (0)
48. (8) : $[Ti(H_2O)_6]^{2+}$ is a $3d^2$ system. In an octahedral system there are three (d_{xy}, d_{yz}, d_{xz}) lower energy levels with energy $-0.4\Delta_o$. As only two of these energy levels of t_{2g} are occupied, so, CFSE = $2(-0.4\Delta_o) = -0.8\Delta_o$
- Hence, $n \times 10^{-1}\Delta_o = 8 \times 10^{-1}\Delta_o$
49. (4) :
- $\begin{array}{c} CH_3-CH-CH_3 \\ | \\ I \end{array} \xrightarrow{\text{alc. KOH}} CH_2=CH-CH_3 \quad (\text{X})$
- $\downarrow \text{NBS, } h\nu, \Delta$
- $CH_2=CH-CH_2Br \quad (\text{Y})$
- $\downarrow \text{alc. KCN}$
- $CH_2=\underset{\text{CN}}{\overset{|}{C}}H-CH_2CN \quad (\text{Z})$
- $\xleftarrow{Br_2}$
- $\begin{array}{c} CH_2-CH-CH_2 \\ | \quad | \quad | \\ Br \quad Br \quad CN \end{array} \quad (\text{Z'})$
50. (5) : Since the hydrocarbon (X) gives only a single monochloride, it implies that all the C—H bonds must be of the same type. So, the given hydrocarbon should be cyclopentane.



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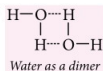
The best questions and their solutions will be printed in this column each month.

- Q1. With how many other water molecules can a water molecule combine by forming hydrogen bonds? Explain with structures in all phases.**

– Dhanraj Hirpara, Gujarat

Ans. Water is the only substance that exists naturally on Earth in all three physical states of matter — gas, liquid and solid and it is always on the move among them. Water molecules are polar molecules having bent shape in which two hydrogen atoms bearing partial positive charge (δ^+) are bonded to one oxygen atom bearing partial negative charge (δ^-).

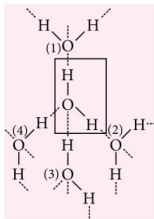
Two water molecules can form hydrogen bonds between them, and exist as *water dimer*.



Hydrogen bonds are weaker and therefore, longer than the covalent bonds.

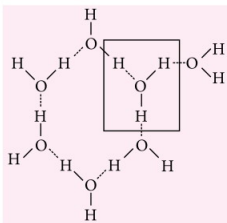
(i) **Hydrogen bonding in liquid water :** Water is unique because its

oxygen atom has two lone pairs and two hydrogen atoms, means that the total number of bonds a water molecule can form is upto 4 (high b.pt. of water is due to large number of H-bonds, each molecule can form).



Hence, liquid water contains about 4-8 water molecules associated by H-bonding gives an open-cage like structure.

(ii) **Hydrogen bonding in ice :** Hydrogen bonding strongly affects the crystal structure of ice. In ice, each molecule of water is surrounded by three water molecules, helping to create an open hexagonal honey-comb lattice.



The density of ice is less than that of water at the same temperature. Thus, ice floats on water.

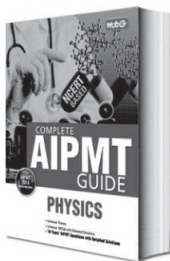
(iii) **Hydrogen bonding in water vapour :** When water is heated, the water molecules move faster as they absorb more heat energy. When the molecules absorb enough energy, those on the surface break free in to the gaseous phase of steam. There is *no hydrogen bonding in water vapour*.

- Q2. Why do clothes made from cellulose wrinkle?**

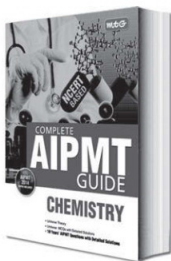
– Himesh Sharma, Delhi

Ans. Polymers are the key to understanding wrinkling. In clothes made from cellulose such as cotton, linen and rayon, the two primary causes of wrinkling are water moisture and heat. The polymers in these fabrics are linked by hydrogen bonds, which are the same bonds that hold together molecules of water. Absorbent fabrics allow water molecules to penetrate the areas between the polymer chains, permitting the formation of new hydrogen bonds. As the fabric cools, new bonds are formed, locking the fibers into a new shape in form of wrinkle.

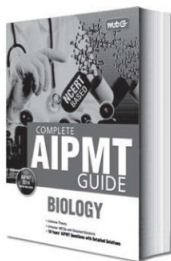
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SOLVED PAPER 2014

AMU (Engineering)

1. On complete combustion, 0.246 g of an organic compound gave 0.198 g of CO_2 and 0.1014 g of H_2O . The ratio of carbon and hydrogen atoms in the compound is

(a) 1 : 3 (b) 1 : 2
(c) 2 : 5 (d) 2 : 7

2. The correct order of basic strength in aqueous solution is

(a) $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N}$
(b) $(\text{CH}_3)_3\text{N} > (\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2$
(c) $\text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N} > (\text{CH}_3)_2\text{NH}$
(d) $(\text{CH}_3)_3\text{N} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_2\text{NH}$

3. $n\text{-C}_7\text{H}_{16} \xrightarrow[10-20 \text{ atm}]{\text{V}_2\text{O}_5, 500^\circ\text{C}} \text{A} \xrightarrow[\text{Cl}_2/h\nu]{\text{Cl}_2/h\nu} \text{B}$

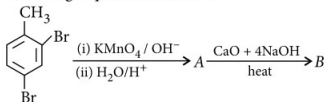
What is B in the above reaction?

(a) Benzyl chloride (b) Benzal chloride
(c) Hexachlorobenzene
(d) Benzene hexachloride

4. What will be the product/s if benzal chloride is heated with a concentrated aqueous KOH solution?

(a) Benzaldehyde
(b) Benzoic acid
(c) Benzyl alcohol and sodium benzoate
(d) An aldol

5. What will be the end product (B) in the following sequence of reactions?

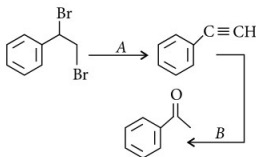


(a) 1, 2-Dibromobenzene
(b) 1, 2-Dibromobenzaldehyde
(c) 1, 3-Dibromobenzene
(d) 1, 4-Dibromobenzene

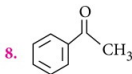
6. The monosaccharide constituents of lactose are

(a) α -D-Glucose and β -D-fructose
(b) α -D-Glucose only
(c) β -D-Glucose only
(d) β -D-Glucose and β -D-galactose.

7. Identify the reagents in the following transformations :



(a) Alc. KOH and H_2O , HgSO_4 , H_2SO_4
(b) Alc. KOH and KMnO_4/H^+
(c) NaNH_2 and H_2O , HgSO_4 , H_2SO_4
(d) NaNH_2 and KMnO_4/H^+



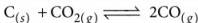
The above ketone will not be formed by

(a) reaction of benzene and acetyl chloride in the presence of AlCl_3
(b) reaction of acetonitrile with phenyl magnesium bromide in ether followed by hydrolysis
(c) treatment of acetyl chloride with dibenzyl cadmium
(d) addition of water to phenylacetylene in the presence of mercuric sulphate and dilute sulphuric acid.

9. What shall be the pH of a solution formed by mixing 10 mL of 0.1 M H_2SO_4 and 10 mL of $\frac{N}{10}$ KOH?

(a) 11.40 (b) 8.64
(c) 3.00 (d) 7.00

10. In the reaction at constant volume,



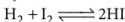
argon gas is added which does not take part in the reaction; choose the correct statement.

- (a) The equilibrium constant is unchanged.
(b) The equilibrium shifts in the forward direction.
(c) The equilibrium shifts in the backward direction.
(d) The direction of equilibrium depends on the amount of argon added.

11. The Balmer series in atomic hydrogen is observed in the following spectral region

(a) Infrared (b) Ultraviolet
(c) Visible (d) Far IR.

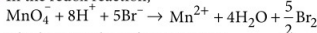
12. The K_p value for the reaction,



at 460 °C is 49. If the initial pressure of H_2 and I_2 is 0.5 atm respectively, what will be the partial pressure of H_2 at equilibrium?

(a) 0.111 atm (b) 0.123 atm
(c) 0.133 atm (d) 0.222 atm

13. In the redox reaction,



which one is the reducing agent?

(a) H^+ (b) MnO_4^-
(c) Br^- (d) Mn^{2+}

14. The rate constant (k_1) of one of the reaction is found to be double that of the rate constant (k_2) of another reaction. The relationship between the corresponding activation energies of the two reactions E_{a_1} and E_{a_2} will be

(a) $E_{a_1} < E_{a_2}$ (b) $E_{a_1} > E_{a_2}$
(c) $E_{a_1} = E_{a_2}$ (d) $E_{a_1} = 2E_{a_2}$

15. The energy required to remove an electron from metal X is $E = 3.31 \times 10^{-20}$ J. Calculate the maximum wavelength of light that can photo eject an electron from metal X.

(a) 6.01×10^{-6} m (b) 3.01×10^{-3} m
(c) 5.01×10^{-6} m (d) None of the above.

16. A 5.82 g silver coin is dissolved in nitric acid. When sodium chloride is added to the solution, all the silver is precipitated as AgCl. The AgCl precipitate weighs 7.20 g. The percentage of silver in the coin is

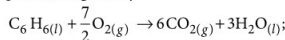
(a) 60.3% (b) 80%
(c) 93.1% (d) 70%

17. For a reaction taking place in three steps, the rate constants are k_1 , k_2 and k_3 and overall rate constant is $k = \frac{k_1 k_3}{k_2}$. If the energies

of activation E_1 , E_2 and E_3 are 60, 30 and 10 kJ mol⁻¹ respectively, then the overall energy of activation is

(a) 30 kJ mol⁻¹ (b) 40 kJ mol⁻¹
(c) 60 kJ mol⁻¹ (d) 100 kJ mol⁻¹

18. At 25°C, for the combustion of 1 mole of liquid benzene, the heat of reaction at constant pressure is given by



$$\Delta H = 780980 \text{ cal}$$

Calculate the heat of reaction at constant volume.

(a) 780.086 kcal (b) -780.086 kcal
(c) -390.043 kcal (d) 390.043 kcal

19. What will be solubility product of $\text{Ca}(\text{OH})_2$ if its solubility is $\sqrt{3}$?

(a) 3 (b) $3\sqrt{3}$
(c) $12\sqrt{3}$ (d) 27

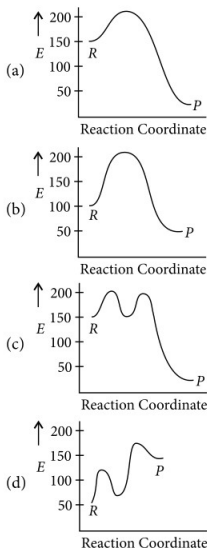
20. 25 mL of 3.0 M HCl are mixed with 75 mL of 4.0 M HCl. If the volumes are additive, the molarity of the final mixture will be

(a) 4.0 M (b) 3.75 M
(c) 4.25 M (d) 3.50 M

21. An exothermic chemical reaction proceeds in two stages:



The activation energy of stage I is 50 kJ mol⁻¹. The enthalpy change of the reaction is -100 kJ mol⁻¹. Identify the energy level diagram for the reaction.



22. Given the reduction potentials of Na^+ , Mg^{2+} , Al^{3+} and Ag^+ as
- | | |
|--|--|
| $E^\circ_{\text{Na}^+/\text{Na}} = -2.71 \text{ V}$ | $E^\circ_{\text{Mg}^{2+}/\text{Mg}} = -2.37 \text{ V}$ |
| $E^\circ_{\text{Al}^{3+}/\text{Al}} = -1.66 \text{ V}$ | $E^\circ_{\text{Ag}^+/\text{Ag}} = 0.80 \text{ V}$ |
- The least stable oxide is
- (a) Ag_2O (b) Al_2O_3
(c) MgO (d) Na_2O
23. The depression in freezing point of water observed for the same amount of acetic acid (I), trichloroacetic acid (II) and trifluoroacetic acid (III) decreases in the order
- (a) $\text{I} > \text{II} > \text{III}$ (b) $\text{II} > \text{I} > \text{III}$
(c) $\text{III} > \text{I} > \text{II}$ (d) $\text{III} > \text{II} > \text{I}$
24. The first ionization potential of Na, Mg and Si are respectively 496, 737 and 786 kJ mol^{-1} . The ionization potential of Al will be closer to
- (a) 760 kJ mol^{-1} (b) 575 kJ mol^{-1}
(c) 801 kJ mol^{-1} (d) 419 kJ mol^{-1}

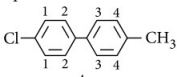
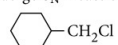




25. Television picture tube is basically
- (a) cathode ray tube (b) anode ray tube
(c) hybrid of cathode and anode tube
(d) none of the above.
26. The television picture on the screen results due to the phenomenon called
- (a) phosphorescence (b) fluorescence
(c) chemofluorescence
(d) fluorophosphorescence.
27. The correct symbol of the species with number of electrons, protons and neutrons as 18, 16 and 16 respectively is
- (a) $^{32}_{16}\text{S}$ (b) $^{32}_{18}\text{S}$ (c) $^{32}_{16}\text{S}^{2-}$ (d) $^{32}_{18}\text{S}^{2-}$
28. Which one of the following is least covalent in nature?
- (a) NF_3 (b) BiF_3 (c) PF_3 (d) SbF_3
29. Which one of the following acids is used as an oxidizer in rocket fuel?
- (a) HClO_4 (b) HNO_2
(c) H_3PO_4 (d) HNO_3
30. The paramagnetic species in the following is
- (a) S_8 (b) S_6 (c) S_2 (d) S_2^{2-}
31. The spin only magnetic moment value (in B.M. unit) of $\text{Cr}(\text{CO})_6$ is
- (a) Zero (b) 2.84 (c) 4.90 (d) 5.92
32. Which one of the following oxidation states is not possible in metal carbonyls?
- (a) +1 (b) 0 (c) -1 (d) +2
33. The lanthanoid which exhibits +4 oxidation state is
- (a) Pm (b) Sm (c) Ce (d) Gd
34. The production of dihydrogen gas via water-gas shift reaction :
- $$\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \xrightarrow[\text{Catalyst}]{\Delta} \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$$
- The CO_2 gas is removed by scrubbing with solution of
- (a) sodium arsenite (b) calcium oxide
(c) sodium phosphite (d) aluminium oxide.
35. How many hydrogen-bonded water molecule(s) are associated in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$?
- (a) 5 (b) 1 (c) 4 (d) 3

36. The ratio of magnetic moment (spin only value) between $[\text{FeF}_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ is approximately
(a) 4 (b) 2 (c) 5 (d) 3
37. Which is not true for describing the catalytic activity of transition metals?
(a) Their ability to adopt multiple oxidation states.
(b) Their ability to form bonds between reactant molecule and atoms of the surface of catalysts.
(c) Increasing the concentration of reactants at the catalyst surface.
(d) Strengthening the bonds in the reacting molecules.
38. The bond order between Ni—C bond in $\text{Ni}(\text{CO})_4$ is
(a) one (b) two
(c) less than two (d) more than two.
39. The interhalogen having dimeric structure is
(a) ClF_3 (b) BrF_3 (c) IF_3 (d) ICl_3
40. Which one of the following transition element has the lowest value of enthalpy of atomization?
(a) Cr (b) Cu (c) Zn (d) Mn
41. Which of the following stability order is correct?
(a) $\text{O}_2^{2-} > \text{O}_2^- > \text{O}_2 > \text{O}_2^+$
(b) $\text{O}_2^+ > \text{O}_2 > \text{O}_2^- > \text{O}_2^{2-}$
(c) $\text{O}_2^+ > \text{O}_2 < \text{O}_2^- > \text{O}_2^{2-}$
(d) $\text{O}_2 > \text{O}_2^+ > \text{O}_2^- > \text{O}_2^{2-}$
42. The IUPAC name of the following compound is

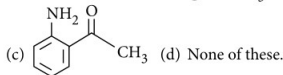
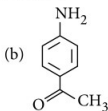
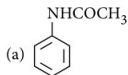
$$\begin{array}{c} \text{CH}_2 - \text{CH} - \text{CH}_2 \\ | \quad | \quad | \\ \text{CN} \quad \text{CN} \quad \text{CN} \end{array}$$

 (a) 1, 2, 3-tricyanopropane
 (b) propane, 1, 2, 3-trinitrile
 (c) 3-cyanopentane-1, 5-dinitrile
 (d) 1, 3, 5-pentanetrinitrile.
43. Which is the least stable carbocation?
 (I) $\text{CH}_3\text{CH}_2\text{CH}_2^+$ (II) $\text{CH}_3\text{CHCH}_3^+$
 (III) $(\text{CH}_3)_3\text{C}^+$ (IV) $(\text{CH}_3)_3\text{CCH}_2^+$
 (a) I (b) II (c) III (d) IV
44. The order of compounds in their reactivity towards HCN is
 (a) Acetaldehyde < Acetone < Methyl *tert*-butyl ketone < Di-*tert*-butyl ketone
 (b) Di-*tert*-butyl ketone < Methyl *tert*-butyl ketone < Acetone < Acetaldehyde
 (c) Di-*tert*-butyl ketone < Acetone < Methyl *tert*-butyl ketone < Acetaldehyde
 (d) Acetone < Acetaldehyde < Di-*tert*-butyl ketone < Methyl *tert*-butyl ketone.
45. The product/s of following reaction is (are)

$$\text{C}_2\text{H}_5\text{Br} + 2\text{Na} + \text{CH}_3\text{Br} \xrightarrow{\text{dry ether}} ?$$

 (a) Ethane (b) Propane
 (c) Butane
 (d) Ethane, propane and butane.
46. Amongst the following, the most basic compound is
 (a) benzylamine (b) aniline
 (c) acetanilide (d) *p*-nitroaniline.
47. Electrophilic substitution of compound A will be fastest at position _____.

 (a) 1 (b) 2 (c) 3 (d) 4
48. Which of the following haloalkanes will undergo $\text{S}_{\text{N}}2$ reaction faster?
 I.  II. 
 III.  IV. 
 (a) I (b) II (c) III (d) IV
49. Propene was oxidised by aqueous KMnO_4 to give a compound (A). Treatment of compound (A) with thionyl chloride gave
 (a) 1, 2-dichloropropane
 (b) 1-chloropropanone
 (c) 2-chloropropanoic acid
 (d) 2-chloropropanal.
50.  $\xrightarrow{\text{CH}_3\text{COCl}, \text{AlCl}_3} ?$

What product will be obtained?



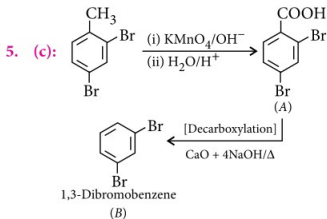
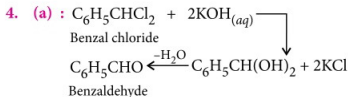
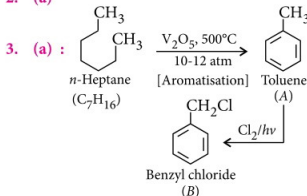
(d) None of these.

SOLUTIONS

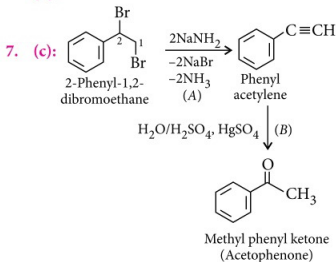
1. (c): Mass of CO_2 formed = 0.198 g
 Mass of H_2O formed = 0.1014 g
 Mass of organic compound taken = 0.246 g
- $$\% \text{ of C} = \frac{12}{44} \times \frac{\text{Mass of } \text{CO}_2}{\text{Mass of compound}} \times 100$$
- $$= \frac{12}{44} \times \frac{0.198}{0.246} \times 100 = 21.95\%$$
- $$\% \text{ of H} = \frac{2}{18} \times \frac{\text{Mass of } \text{H}_2\text{O}}{\text{Mass of compound}} \times 100$$
- $$= \frac{2}{18} \times \frac{0.1014}{0.246} \times 100 = 4.58\%$$

Element	Percentage	At. mass	Relative no. of atoms	Ratio
C	21.95	12	$\frac{21.95}{12} = 1.83$	1.83 ~ 2.0
H	4.58	1	$\frac{4.58}{1} = 4.58$	4.58 ~ 5.0

2. (a)



6. (d)

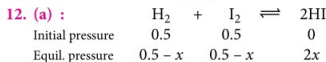


8. (c)

9. (c)

10. (a)

11. (c)



$$\text{Thus, } K_p = \frac{(p_{\text{HI}})^2}{(p_{\text{H}_2})(p_{\text{I}_2})}$$

$$49 = \frac{(2x)^2}{(0.5-x)(0.5-x)}$$

$$7 = \frac{2x}{(0.5-x)} \Rightarrow x = 0.389$$

$$p_{\text{H}_2} = 0.5 - x = 0.5 - 0.389 = 0.111 \text{ atm}$$

13. (c)

14. (a): According to Arrhenius equation,

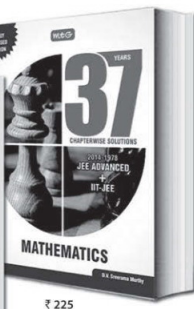
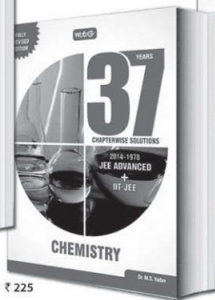
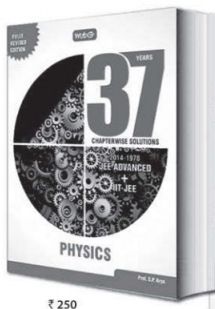
$$k = Ae^{-E_a/RT}$$

$$k_1 = Ae^{-E_{a1}/RT} \quad \dots (i)$$

$$k_2 = Ae^{-E_{a2}/RT} \quad \dots (ii)$$

On dividing equation (i) by (ii), we get

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$$\frac{k_1}{k_2} = e^{(-E_{a_1} + E_{a_2})/RT}$$

$$\frac{2k_2}{k_2} = e^{(E_{a_2} - E_{a_1})/RT}$$

$$2 = e^{(E_{a_2} - E_{a_1})/RT}$$

$$\ln 2 = \frac{E_{a_2} - E_{a_1}}{RT}$$

$$0.693 = \frac{E_{a_2} - E_{a_1}}{RT}$$

$$E_{a_2} - E_{a_1} = +ve, \text{ thus, } E_{a_2} > E_{a_1}$$

15. (a) : $E = 3.31 \times 10^{-20} \text{ J}, \lambda = ?$

$$E = \frac{hc}{\lambda} = \frac{6.62 \times 10^{-34} \times 3 \times 10^8}{\lambda}$$

$$3.31 \times 10^{-20} = \frac{6.62 \times 10^{-34} \times 3 \times 10^8}{\lambda}$$

$$\lambda = 2 \times 10^{-34} \times 10^{20} \times 3 \times 10^8 = 6 \times 10^{-6} \text{ m}$$

16. (c): Fraction of Ag in $\text{AgCl} = \frac{107.9}{143.3} = 0.753$

$$\text{Wt. of Ag in AgCl} = 0.753 \times 7.20 = 5.42 \text{ g}$$

$$\text{Hence, 5.82 g coin contains 5.42 g of Ag}$$

$$\text{Now, fraction of Ag in coin} = \frac{5.42}{5.82} = 0.931 \text{ g}$$

$$\% \text{ of Ag in the coin} = 93.1\%$$

17. (b) : $k_1 = A_1 e^{-E_{a_1}/RT}$

$$k_2 = A_2 e^{-E_{a_2}/RT}; k_3 = A_3 e^{-E_{a_3}/RT}$$

$$\text{Since, } k = \frac{k_1 k_3}{k_2} = \left(\frac{A_1 A_3}{A_2} \right) e^{-(E_{a_1} + E_{a_3} - E_{a_2})/RT}$$

$$\therefore E_{a(\text{total})} = E_{a_1} + E_{a_3} - E_{a_2} = 60 + 10 - 30 = 40 \text{ kJ mol}^{-1}$$

18. (b) : $\Delta H = \Delta E + \Delta n_g RT$

$$\Delta n_g = n_p - n_R = 6 - \frac{7}{2} = 2.5$$

$$\text{Thus, } \Delta E = \Delta H - \Delta n_g RT \quad (\because \Delta_c H = -ve)$$

$$= -780980 - (2.5) \times (2 \times 298)$$

$$= -782470 \text{ cal}$$

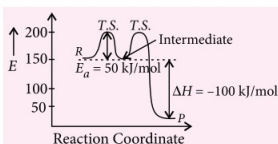
$$= -782.470 \text{ kcal} \approx -780.086 \text{ kcal}$$

19. (c)

20. (b) : If two solutions containing same solute are mixed, then molarity of the resulting solution will be

$$M = \frac{M_1 V_1 + M_2 V_2}{(V_1 + V_2)} = \frac{3 \times 25 + 4 \times 75}{25 + 75} = 3.75 \text{ M}$$

21. (c):



For graph (c), activation energy,

$$E_a = E_{(\text{activated complex})} - E_{(\text{ground state})} = 200 - 150 = 50 \text{ kJ/mol (for stage I)}$$

$$\Delta H = E_f - E_b$$

$$-100 = 50 - E_b$$

$$E_b = 150 \text{ kJ/mol}$$

22. (a)

23. (d) : Among H, Cl and F, fluorine is the most electronegative. Thus, trifluoroacetic acid can easily lose H^+ ions i.e. more and more ionised. This increases the van't Hoff factor (i) as well as the colligative property (i.e. depression in freezing point).

$$\Delta T_f \propto i \cdot K_f \cdot m$$

Therefore, the decreasing order is $\text{III} > \text{II} > \text{I}$.

24. (b) : In case of Mg, it has $3s^2$ electrons whereas in Al, it has $3s^2 3p^1$ electrons.

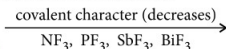
The value of IE_1 of Al will be more closer to 575 kJ/mol or lower than Mg (i.e. < 737 kJ/mol) because of effective shielding of $3p$ electrons from the nucleus by $3s$ -electrons.

25. (a) : The CRT (cathode ray tube) is basically the picture tube of a television set.

26. (b)

27. (c)

28. (b) : On moving down the group, the covalent character of halides decreases.



29. (d)

30. (c): In vapour state, sulphur partly exists as S_2 molecule which has two unpaired electrons in the antibonding π^* orbitals like O_2 and, hence, exhibits paramagnetism.

31. (a)

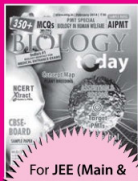
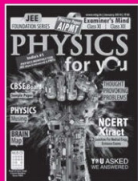
32. (d) : In metal carbonyls, metal uses d -electrons, and the metal should be in a relatively low oxidation state (< +2), to make the back donation process favourable.

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